Journal of
Inorganic & Nuclear Chemistry

VOLUME 17 1961

VOL.
17
1961

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 1 to 5. Pergamon Press Ltd.

α-PARTICLE BRANCHING RATIOS FOR NEUTRON-DEFICIENT ASTATINE ISOTOPES*

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(*Received* 12 *July* 1960; *in revised form* 17 *August* 1960)

Abstract—The ratio of the number of α-particle disintegrations to the total number of disintegrations (α-branching ratio) has been measured for the isotopes $^{202-206}$At. The values of these ratios are 0·120 for ^{202}At, 0·138 for ^{203}At, 0·0452 for ^{204}At, 0·184 for ^{205}At and 0·0088 for ^{206}At. The over-all half-lives measured for these isotopes are in agreement with previously reported values except for that of ^{206}At, which was found to have a half-life of 29·5 min rather than the reported 22 min.

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BY bombarding ^{209}Bi with ^{4}He particles of energies from 60 to 275 MeV, BARTON *et al.* produced and studied the properties of several astatine isotopes with mass numbers below 210.[1] Other experimenters, using helium ions incident on bismuth,[2] carbon ions on gold,[3,4] and nitrogen ions on platinum[5] have made similar investigations of the decay properties of the light astatine isotopes.

The work reported here is an investigation of the astatine isotopes of mass numbers 202 to 206. We have measured the ratio of the number of disintegrations by α-particle emission to the total number of disintegrations, or the alpha-branching ratio, for each isotope, and have also tried to establish more positively the half lives and mass assignments of the isotopes.

EXPERIMENTAL PROCEDURE

The astatine isotopes were produced by irradiation of 0·1 mil gold foils with 50–125 MeV ^{12}C ions, and by bombardment of 0·25 mil platinum foils with 65–130 MeV ^{14}N ions from the Berkeley heavy-ion linear accelerator (Hilac).

The astatine was removed from the foils by heating them to red heat in quartz cups and was condensed on a water-cooled aluminium foil. Since it was found that some of the polonium distilled with the astatine, a second distillation was performed. The aluminium foil was gently heated in a second cup with a microburner and the astatine collected on a water-cooled platinum disk. This technique was found to give yields of 50–75 per cent of the astatine and $\leqslant$0·02 per cent of the polonium from the target foils. There was no observable loss of astatine by volatilization from the platinum disks during subsequent counting of the α-particles.

The α-particle radiations were detected in a gridded ionization chamber connected to either a 50- or 100-channel pulse-height analyser. A sufficient number of counts was made to identify the isotopes in question by half life as well as by α-particle energy. In a few cases it was possible to observe the growth of the α-activity due to the polonium daughters from electron-capture decay of the astatine isotopes.

* This work was supported by the U.S. Atomic Energy Commission.

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[1] G. W. BARTON, A. GHIORSO and I. PERLMAN, *Phys. Rev.* **82**, 13 (1951).
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Since α-branching ratios have been reported for ^{202}Po, ^{205}Po and ^{206}Po, it was possible to calculate the α-branching ratios of their parent astatine isotopes from the observed counting rates of the appropriate astatine and polonium alpha groups.[2,6,7] It was necessary to estimate the α-branching ratio of ^{204}Po from α-decay systematics. For ^{203}At, the branching ratio was determined by counting the gamma rays of ^{203}Pb. The results of these measurements together with the polonium and lead branching ratios used are summarized in Table 1.

TABLE 1.—DECAY PROPERTIES OF THE ASTATINE ISOTOPES

Isotope	Half-life (min)	$\frac{\alpha\text{-decay}}{\text{Total disint.}}$	Partial alpha half-life (min)	Basis	Reference No.
^{202}At	3·0 ± 0·2	0·120 ± 0·008	25	α/tot. ^{202}Po 0·02	2
^{203}At	7·4 ± 0·3	0·138 ± 0·006	53·6	^{203}Pb EC	9
^{204}At	9·3 ± 0·3	0·0452 ± 0·004	206	α/tot. ^{204}Po 0·0063	
^{205}At	26·2 ± 0·5	0·184 ± 0·016	142	α/tot. ^{205}Po 0·00074	6
^{206}At	29·5 ± 0·6	0·0088 ± 0·008	$3·32 \times 10^3$	α/tot. ^{206}Po 0·05	7

The over-all half-lives observed are in agreement with those reported by HOFF *et al.*[4], with the exception of that of ^{206}At, which they reported to be 21·5 min and which we have determined to be 29·5 ± 0·6 min. With the exception of ^{206}At, the half lives listed in Table 1 are those reported by HOFF *et al.*

The errors listed in Table 1 for the ratios of number of α-particle disintegrations to total number of disintegrations are standard deviations of several determinations. They do not include the uncertainty in the number of α-particles or γ-rays per disintegration in the appropriate polonium or lead daughter.

RESULTS

^{202}At. An α-activity of half-life 3·0 ± 0·2 min and α-particles of energies 6·231 (36%) and 6·133 MeV (64%) has been attributed by HOFF *et al.*[4] to ^{202}At. The excitation functions for production of astatine isotopes in carbon-ion bombardments of gold are consistent with this mass assignment.[8] Using the reported[2] α-branching ratio of 0·02 for ^{202}Po, we have calculated an alpha-branching ratio of 0·120 ± 0·008 for ^{202}At, corresponding to a partial α-half-life of 25 min.

^{203}At. Irradiating bismuth with 275 MeV ^{4}He ions, BARTON *et al.* observed α-particles of 6·10 MeV energy decaying with a 7 min half-life.[1] They assumed that this activity was due to ^{203}At. BURCHAM and HAYWOOD detected the same activity produced in nitrogen-ion bombardment of platinum.[5] HOFF *et al.* have reported an α-particle energy of 6·086 MeV and a half life of 7·4 ± 0·3 min for this isotope.

When the α-particles due to ^{203}At had been counted, the sample was allowed to decay through ^{203}Po and ^{203}Bi to ^{203}Pb. Attempts to detect alpha particles from both ^{203}Po and ^{203}Bi were unsuccessful and the α-branching ratio for both isotopes was assumed to be small.[8] The 279 keV γ-ray emitted in the decay of ^{203}Pb was detected in a 1½ in. sodium iodide crystal coupled to a photomultiplier tube whose output was

[6] K. L. HALL, UCRL-1460 (1951).
[7] F. F. MOMYER, JR. and E. K. HYDE, *J. Inorg. Chem.* **1**, 274 (1955).
[8] R. M. LATIMER and T. D. THOMAS, (Lawrence Radiation Laboratory), unpublished data.
[9] D. STROMINGER, J. M. HOLLANDER and C. T. SEABORG, *Revs. Mod. Phys.* **30**, 585 (1958).

put into a 100-channel pulse-height analyser. The 279 keV level in ^{203}Tl is populated by 99 per cent of the decay events of ^{203}Pb. The ratio of *K*-electron conversion to *L*-conversion is 3·4. From these data and because the *M*-electron conversion is negligible it is possible to calculate a ratio of 0·83 γ-rays per disintegration of ^{203}Pb.* The ^{203}At α-branching ratio determined on the basis of counting the 279 keV γ-rays is 0·138 $\pm$ 0·006, giving a partial α-half-life of 53·6 min.

^{204}At. On the basis of experiments in which a bismuth fraction was periodically "milked" from astatine produced in the bombardment of bismuth with 150 MeV helium ions, BARTON *et al.*[1] reported a 25 min half-life for ^{204}At. No α-decay was observed from this isotope.

HOFF *et al.* have reported a 5·950 MeV α-group, decaying with a half-life of 9·3 $\pm$ 0·3 min, which they attribute to ^{204}At.[4] They report no evidence for production of a 25 min isomer.

In this study, an α-group of 5·95 MeV energy and half-life of 9 $\pm$ 1 min has been observed. Excitation functions support the assignment of this activity to ^{204}At.[8] The growth of the 5·37 MeV α-group of ^{204}Po, from electron-capture decay of ^{204}At, indicates a parent activity of approximately 9 min half-life. There is no indication of a 25 min component in the growth curve.

An experiment was designed for more careful observation of a 25 min isomer of ^{204}At. A 0·25 mil natural platinum foil was bombarded with nitrogen ions of 59 to 77 MeV energy. The foil was allowed to stand for approximately 45 min after the end of the bombardment in order that the 9·3 min ^{204}At would have essentially completely decayed before separation of the astatine. The astatine fraction was then isolated from the polonium fraction by means of the double-volatilization procedure discussed above. The α-particles emitted by the sample were observed in the α-particle pulse-height analyser, and no growth of ^{204}Po was seen. From the amount of ^{207}At in the sample and the ratio of 9·3 min ^{204}At to ^{207}At produced in other bombardments done under these conditions, it was possible to set an upper limit of 0·07 on the ratio of the yield of 25 min isomer to that of the 9·3-min isomer.

There is already evidence that different methods of production of odd-odd astatine isotopes may yield different isomers. For example, from the decay products of ^{212}Fr, HYDE *et al.* isolated an activity with a half life of 1·7 hr, which they assigned to ^{208}At.[10] BARTON *et al.* produced an activity of 6·3 hr half-life from the helium-ion irradiation of bismuth which they also assigned to ^{208}At. As noted below, there is also evidence for the existence of two isomers of ^{206}At. Similarly, it is possible that two isomers exist for ^{204}At.

The α-branching ratio of ^{204}Po has been estimated by KARRAKER and TEMPLETON to be 0·01 on the basis of a comparison of expected reaction cross-sections and actual yields.[11] A perhaps more accurate value may be estimated by plotting the partial α-half-lives of even-even polonium isotopes versus the inverse square root of the effective α-decay energy.[12] Fig. 1 shows such a plot for the isotopes ^{202}Po, ^{206}Po and ^{208}Po. (Note: The data from ^{210}Po were not used in this analysis because ^{210}Po has a closed shell of neutrons and may, as a result, decay abnormally). By fitting a straight line to the data by least squares, we calculate a value of (3·4 $\pm$ 0·9) $\times$ 10^4 min for the partial

* The various data on the decay of ^{203}Pb have been taken from the compilation by STROMINGER *et al.*[9]

[10] E. K. HYDE, A. GHIORSO and G. T. SEABORG, *Phys. Rev.* **77**, 765 (1950).
[11] D. G. KARRAKER and D. H. TEMPLETON, *Phys. Rev.* **81**, 510 (1951).
[12] C. J. GALLAGHER, JR. and J. O. RASMUSSEN, *J. Inorg. Nucl. Chem.* **3**, 333 (1957).

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α-half-life of ^{204}Po. (The limit of error is the standard deviation calculated from the deviation of the points from the least-squares line). We have determined the total half-life to be 212 ± 2 min (as compared with previously reported values of 228 min[11] and 210 min[5]), giving an α-branching ratio of 0·0063 ± 0·0016 for ^{204}Po. This value together with the number of α-particles emitted by the 9·3 min ^{204}At and its daughter, ^{204}Po, give an α-branching ratio for ^{204}At of 0·0452 ± 0·004 (or 0·045 ± 0·013 if we

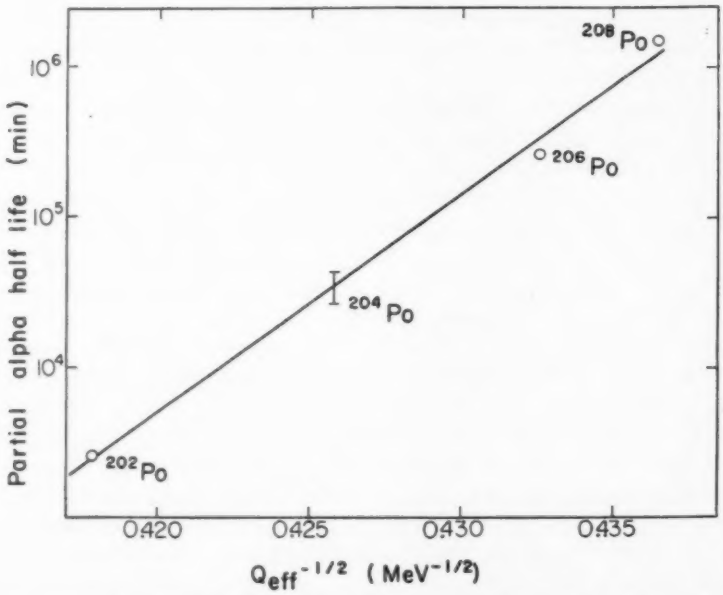

FIG. 1.—Log partial alpha half-life of polonium isotopes with fewer than 126 neutrons plotted against $Q_{ett}^{-\frac{1}{2}}$. Q_{ett} is the effective α-particle-decay energy as defined by GALLAGHER and RASMUSSEN.[12] The circles are the values given by STROMINGER *et al.*[9] and the line has been fitted to the points by least squares. The line shown for ^{204}Po is based on the least-squares fit.

include the error in the ^{204}Po branching ratio). The corresponding value of the partial alpha half-life of ^{204}At is 206 min.

^{205}At. By milking experiments and by α-counting, BARTON *et al.* concluded that ^{205}At has a half-life of 25 min and an α-particle energy of 5·90 MeV.[1] The same activity has been reported by BURCHAM and HAYWOOD[5]. HOFF *et al.* have assigned the values of 26·2 ± 0·5 min and 5·899 MeV for the half-life and energy, respectively.[4]

Because of the low α-branching ratio of ^{205}Po (0·074 per cent[6]) it has not been possible to see clearly the growth of ^{205}Po α-activity from the decay of ^{205}At. However, from the ^{205}Po activity observed in long counts and the α-branching ratio mentioned above, it has been possible to calculate an α-branching ratio of 0·184 ± 0·016 for ^{205}At, corresponding to a partial α-half-life of 142 min.

^{206}At. On the basis of "milking" experiments, BARTON *et al.*[1] and STONER[2] reported half-lives of 2·6 and 2·9 hr, respectively, for ^{206}At. They did not observe any radiations attributable to ^{206}At.

HOFF *et al.* report no evidence for such an activity and have assigned an α-activity

of 5·699 MeV energy and half life of 21·7 ± 2·6 min to ^{206}At. The excitation functions of platinum bombarded with nitrogen ions are consistent with this mass assignment.[13]

In the present study, the resolution of the α-particle pulse-height analyser was not good enough to clearly separate the 5·7 MeV α-group emitted by ^{206}At from the 5·75 MeV particles of ^{207}At. Thus the combined activities were observed as a function of time and resolved by analysis of the decay curve. A least-squares analysis of several of the curves for which the statistics were good yielded a value of 29·5 ± 0·6 min for the half-life of ^{206}At.

The α-branching ratio was determined by counting the α-particles of ^{206}Po several hours after isolation of the astatine. In calculating the ^{206}At branching ratio, we used values of 8·8 days[14] for the ^{206}Po half-life and 0·05[7] for the α-branching ratio. The value obtained is 0·0088 ± 0·0008, giving a partial α-half-life of $3{\cdot}32 \times 10^3$ min.

No evidence for production of a longer-lived isomer of ^{206}At was observed. Since the counting rates obtained from the alpha particles of ^{206}Po were always quite low, it was not possible to observe its growth. Thus an experiment similar to that described above in the discussion of ^{204}Po was designed specifically to look for any long-lived ^{206}At isomer. A stack of foils consisting of three electroplated platinum targets (enriched in ^{198}Pt) on 0·1 mil Ag backing foil was bombarded for 3 hr. The platinum target material faced away from the impinging beam, and the recoiling astatine products were stopped in 0·25 mil Al catcher foils. At the end of bombardment, the recoil catchers were divided into two portions. The astatine fraction from one portion of each recoil catcher was isolated approximately 20 min after the end of the bombardment, and decay of the various astatine isotopes was followed in the α-particle pulse-height analyzer. About 2 hr later, astatine from the other portions of the catchers was separated and the samples were pulse-height analysed. Later, the α-particle radiations emitted by all the samples were counted for long periods of time in order to obtain good statistics on the amount of ^{206}Po on each. The samples from the two halves of each recoil catcher were normalized to the same chemical yields by use of the amounts of ^{205}At activity observed on each in the early, short counts. The results of this experiment make it possible to set the following upper limits on the ratios of 2·6 hr ^{206}At to 29·5 min ^{206}At produced at the indicated ^{14}N bombarding energies: 75 MeV, 0·04; 91·5 MeV, 0·022; 103 MeV, 0·031.

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THE NEUTRON CAPTURE CROSS-SECTIONS OF ^{149}Sm AND ^{150}Sm

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(*Received* 7 *August* 1960)

Abstract—The effective neutron cross-section of ^{149}Sm has been determined in three different reactor positions by measuring mass spectrometrically the amount of ^{150}Sm formed by neutron capture. Analysis of the results shows that the effective cross-section of ^{149}Sm in a well-thermalized neutron spectrum of known temperature can be calculated to within ± 2 per cent. The cross section of ^{150}Sm in a thermalized spectrum at 50°C with $r = 0{\cdot}0015$ is found to be 102 ± 5 barns.

THE stable nuclide ^{149}Sm is an important fission product poison and the exact calculation of its neutron absorption under any given conditions is of interest in connection with reactivity changes. Several workers have determined 'pile neutron' cross-sections[1–3] but such results are of limited value since the cross-section is highly dependent on neutron temperature. In the present work the cross-section has been measured in three well-characterised reactor spectra; the results are compared with other data obtained in known spectra at the end of the paper.

EXPERIMENTAL

The determinations were based on the mass-spectrometric measurement of the ^{150}Sm produced on irradiating "foils" of samarium electromagnetically enriched in the 149 isotope. If $^{149}N_0$, $^{150}N_0$, $^{149}N_F$ and $^{150}N_F$ represent the original and final numbers of the appropriate atoms, then with $R_0 = {}^{150}N_0/{}^{149}N_0$ and $R_F = {}^{150}N_F/{}^{149}N_F$ it can easily be shown that

$$(R_F + 1)/(R_0 + 1) = \exp i\hat{\sigma} \qquad (1)$$

where i is the integrated neutron flux and $\hat{\sigma}$ is the effective cross-section of ^{149}Sm. This equation is simple because capture by ^{148}Sm and ^{150}Sm is negligible compared with capture by ^{149}Sm.[3] The factor i was obtained by the simultaneous irradiation of cobalt monitors.

Three separate irradiations were performed, the samarium and cobalt being contained in aluminium cans 7·5 cm high and 2·5 cm diameter. In experiment 1 samples of samarium and cobalt were contained in a 0·036″ thick cadmium 'pill' box ($\frac{1}{2}$″ × $\frac{1}{2}$″ diameter) at the bottom of the can; two other cobalt wires and another samarium sample were also placed in the can, being separated from the cadmium box and from each other by cylinders of graphite (see Table 1). The irradiation was carried out in the core of BEPO for 14 days with a flux of $\sim 10^{12}$ neutrons/cm^{-2} sec^{-1}. No cadmium was used in experiments 2 and 3; alternate samples of samarium and cobalt were separated by cylinders of graphite. Both these irradiations were performed in the graphite reflector of BEPO; experiment 2 took 36 days in a flux of $\sim 5 \times 10^{11}$ neutrons cm^{-2} sec^{-1}, and experiment 3 took 180 days in a flux of $\sim 10^{11}$ neutrons cm^{-2} sec^{-1}.

In order to simplify the chemistry and thus avoid any possible contamination after irradiation, the samarium "foils" were prepared by impregnating 1·2 cm diameter disks of low ash filter paper.

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[1] E. A. MELAIKA, M. J. PARKER, J. A. PETRUSKA and R. H. TOMLINSON, *Canad. J. Chem.* **33**, 830 (1955).
[2] D. J. LITTLER, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, A/CONF. 15/P/11, United Nations (1956).
[3] K. L. AITKEN, D. J. LITTLER, E. E. LOCKETT and G. H. PALMER, *J. Nucl. Energy*, **4**, 33 (1957).

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TABLE 1.—SUMMARY OF EXPERIMENTAL DATA

Exp No.	T (°C)	r, from Cd ratio data	Sample and distance from base of can (cm)	Atom % of samarium isotope				R_0 or R_F	Monitor activity (mc/mg)	Integrated flux i	Mean ratio	$\hat{\sigma}$ from from eq. (1) (barns)
				148	149	150	151					
			Original a)	0·365	96·585	0·430	0·000	0·00445	—	—	$R_0 = 0·00447$	—
			Sm b)	0·363	96·577	0·433	0·000	0·00448	—	—	$\pm$ 0·00002	—
	130	0·0365	Sm under Cd	0·359	96·58	0·466	—	0·00482	—	—	0·00482	
			Co under Cd	—	—	—	—	—	0·00706			
1			Co 4	—	—	—	—	—	0·0761			
			Sm 5	0·359	84·14	12·90	—	0·1533	—	$1·73 \times 10^{18}$	$R_F = 0·1533$	79,920
			Co 6	—	—	—	—	—	0·0788		$\pm$ 0·004	$\pm$ 2,400
	80	0·0136	Co 0	—	—	—	—	—	0·06855			
			Sm 1				—	0·1339	—			
			Co 2	—	—	—	—	—	0·06807	$1·59 \times 10^{18}$	$R_F = 0·1343$	
2			Sm 3					0·1344			$\pm$ 0·0005	76,430
			Co 4	—	—	—	—	—	0·06750			$\pm$ 2,400
			Sm 5	0·355	85·53	11·52		0·1347				
	50	0·0015	Sm 0	0·363	68·96	28·04	0·006 $\pm$ ·002	0·4066				
			Co 1	—	—	—	—	—	0·1854			
			Sm 2	0·361	68·72	28·33	0·0072 $\pm$ ·0002	0·4123		$4·62 \times 10^{18}$	$R_F = 0·4114$ $\pm$ 0·0005	73,620 $\pm$ 2,400
3			Co 3	—	—	—	—	—	0·1908			
			Sm 4	0·354	68·58	28·48	0·005 $\pm$ ·002	0·4153				
			Co 5	—	—	—	—	—	0·1900			

The enriched samarium nitrate solution supplied by the Electromagnetic Separation Group was diluted to 300 μg/ml; the disks were wetted with 20 μl of this solution and were immediately cooled and vacuum freeze-dried. This procedure ensured a reasonably even distribution of ~6 μg Sm/cm², a "foil" thickness too small to give rise to appreciable neutron self-shielding. For irradiation each loaded disk was sandwiched between two plain filter paper disks and the whole combination was wrapped in 0·0002 in. aluminium foil. After irradiation the slightly carbonised, brittle disks were ashed at 600°C in a platinum crucible; the ash was dissolved in 0·1 ml of 50 per cent nitric acid, evaporated almost to dryness and the resulting residue was dissolved in 50 μl of distilled water. Mass spectrometric analysis was performed on 5 μl of this solution. Analysis of the solution resulting from the application of the above treatment to an unirradiated loaded disk gave the percentage abundances shown in Table 2. The errors quoted are standard deviations from the mean.

TABLE 2.—PERCENTAGE ISOTOPIC COMPOSITION OF SAMARIUM SAMPLES

Mass number	144	147	148	149	150	151	152	154
Original solution	0·041 ± 0·001	1·98 ± 0·01	0·365 ± 0·008	96·58 ± 0·03	0·430 ± 0·006	0·000	0·397 ± 0·005	0·202 ± 0·004
Solution recovered from unirradiated disk	0·042 ± 0·001	1·98 ± 0·01	0·363 ± 0·008	96·56 ± 0·03	0·433 ± 0·006	0·000	0·396 ± 0·005	0·203 ± 0·004
Natural samarium	3·1	15·0	11·2	13·8	7·4	0	26·8	22·7

The mass spectrometer was a prototype for the present Metropolitan-Vickers M.S.5 model, with 12 in. radius and a mass resolution of 1 in 800. The ion source was a multiple filament thermal ionization type;[4] one filament was held at ~1800°K and the other, holding the sample, was warmed until evaporation occurred with subsequent ionisation at the hotter filament. The ion beams were detected with an 11-stage Allen type electron multiplier[5] which was stable for long periods and linear over the range used. Currents were never less than 10^{-15} A. Independent experiments supported the conclusion of PLOCH and WALCHER[6] that the response was inversely proportional to ion velocity; a correction factor of the form $\sqrt{(m_2/m_1)}$ was therefore applied in this work. Fresh filaments were cleaned at 2000°K in vacuum for at least an hour before loading 5 μl of samarium solution (~1 μg Sm). The source was rapidly heated in the spectrometer until ionized samarium was just detectable; the source was left in this condition for 24 hr to remove more easily evaporated materials before the analysis. In some experiments traces of neodymium, apparently of natural isotopic abundance, were detected. The least abundant samarium isotope in the present work was ^{144}Sm (~0·04 per cent); no spectrogram was used in which any of the neodymium mass peaks at 142, 143, 145 and 146 exceeded 10 per cent of this value; even so, appropriate corrections for the presence of neodymium were made. The samples were not exhausted after several hours of full-scale running, which was ample time to take up to forty spectrograms. One sample in experiment 3 was carefully examined for mass 151. The peak at this mass was compared with the peak for mass 152 at a greatly-increased ion emission; peaks at masses 152 and 150 were compared at normal emission, the product giving the mass ratio 151/150. Appropriate "background" corrections were made when comparing peaks at masses 151 and 152.

Johnson Matthey's "Specpure" cobalt wire, diameter 0·005 in. and mass ~1–1·6 mgm, was used as the flux monitor. The same wire was also used both free and wrapped in cadmium to determine before irradiation the ratio of epithermal to thermal neutrons in the irradiation positions used. Similar wires of diameter 0·001, 0·005, 0·010 and 0·020 in. were used in earlier experiments to measure the extent of neutron self-shielding; this was determined by extrapolating to zero diameter the curves relating activity per unit weight and diameter for different wires irradiated together. The mass of each wire was measured on a quartz fibre ultra-microbalance[7] using platinum weights which were calibrated against an NPL 50 mg weight. Each wire was wrapped in two layers of 0·0002 in. aluminium foil before irradiation. After irradiation the monitors were allowed to decay for at least a week to ensure that no significant activity arose from the aluminium foil; without removing the foil

[4] M. G. INGHRAM and W. A. CHUPKA, *Rev. Sci. Instrum.* **24**, 518 (1953).
[5] J. S. ALLEN, *Rev. Sci. Instrum.* **18**, 739 (1957).
[6] W. PLOCH and W. WALCHER, *Rev. Sci. Instr.* **22**, 1028 (1951).
[7] H. CARMICHAEL, *Canad. J. Phys.* **30**, 524 (1952).

each monitor was carefully compared with a radium source in a pressurized argon ionization chamber.[8] The radium source had previously been compared with active cobalt wires which were subsequently dissolved and assayed for radioactivity by β–γ-coincidence counting.[9]

RESULTS

The measured activity of each cobalt wire monitor was subject to two corrections. Firstly, correction was made for decay over the period from cessation of irradiation to actual measurement (1–4 weeks). The half life of ^{60}Co has been taken as $5{\cdot}26 \pm 0{\cdot}03$ years.[10] Secondly, correction was made for "self-shielding" in the 0·005 in. diameter cobalt wires; the correction factors, derived from earlier experiments, were 1·046, 1·026 and 1·022 for experiments 1, 2 and 3 respectively. The factor for cobalt wires irradiated under 0·036 in. cadmium was 1·285. The integrated neutron flux i, was then calculated from the normal irradiation equation

$$\text{specific activity of monitor} = i\lambda\hat{\sigma}\left[1 - \frac{(i\hat{\sigma} + \lambda t)}{2} + \frac{(\lambda t)^2 + (\lambda t)(i\hat{\sigma}) + (i\hat{\sigma})^2}{6}\right] \quad (2)$$

by successive approximation. The quantity t is the total time in the reactor. The effective cross section $\hat{\sigma}$ was derived from the equation

$$\hat{\sigma} = \sigma_0(g + rs) \quad (3)$$

where σ_0 is the 2200 m/sec cross-section, and g and s are functions of neutron temperature depending on departure from the $1/v$ law.[11] For cobalt g is unity and

$$s = \frac{57{\cdot}1}{\sigma_0}\sqrt{\left(\frac{4\mathrm{IT}}{\pi \mathrm{I}_{10}}\right)}$$

57·1 barns representing the non-$1/v$ part of the resonance integral;[12] σ_0 was taken as $36{\cdot}6 \pm 0{\cdot}4$ barns.[13] The parameter r was obtained from cadmium ratio measurements with cobalt monitors in the same irradiation positions as in the three experiments, using the equation

$$(1 + rs)/rR_{\mathrm{Cd}} = s + T^{\frac{1}{2}}/KT_0^{\frac{1}{2}} \quad (4)$$

where R_{Cd} is the cadmium ratio, and K was taken as 2·25.[11] The "neutron temperature," T, was assumed to be 130°, 80° and 50°C[14] in the three experiments respectively since the moderator temperature at the irradiation positions were 80°, 50° and 30°C.[15] Many uncertainties which are not easily subject to evaluation enter into the calculation of i; these include errors in the absolute standardization and half-life of ^{60}Co, the cross-section of ^{59}Co and the experimental measurements themselves. It seems likely that the standard error on values of i is $\sim\pm 2{\cdot}5$ per cent. The error introduced in the calculation of $\hat{\sigma}$ for ^{149}Sm by uncertainties in the mass analysis leads to an overall standard error of $\sim\pm 3$ per cent.

[8] K. L. Aitken and F. W. Cornish, U.K.A.E.A. Report AERE/C/R 2627 (1958).
[9] B. Slade, Private communication (1959).
[10] W. E. Perry. Private communication (1959).
[11] C. H. Westcott, W. H. Walker and T. K. Alexander, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/202. United Nations (1959).
[12] T. A. Eastwood and R. D. Werner, Canadian Atomic Energy Report, CI-207 (1959).
[13] C. H. Westcott, Canadian Atomic Energy Report, CRRP-787 (1958).
[14] H. Rose. Private communication (1959).
[15] D. Jefferson-Loveday. Private communication (1959).

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DISCUSSION

As expected, the effective cross-section of ^{149}Sm ($\hat{\sigma}$) varies considerably from one irradiation position to another. That this is due to temperature effects rather than to variation in epi-thermal flux is shown by the results obtained after irradiation under 0·036″ cadmium (experiment 1). The total resonance integral for ^{149}Sm, based on 72·3 barns as the resonance integral of cobalt,[12] is 4,400 barns. The influence of temperature is again brought out in the variation of effective cross-section $\hat{\sigma}$ under different

TABLE 3.—EFFECTIVE CROSS-SECTION OF ^{149}Sm UNDER VARIOUS CONDITIONS AND CALCULATED VALUES OF σ_0

Author	T (°C)	r	$\hat{\sigma}$	σ_0	
				Using WESTCOTT's g & s data[13]	Using PATTENDEN's g & s data[16]
TATTERSALL *et al.*[17]	20	0	68,200	42,100 (±700)	40,500 (±700)
Present work	50	0·0015	73,620	42,600 (±1200)	40,900 (±1200)
TATTERSALL *et al.*[17]	70	0·042	72,200	41,600 (±1000)	39,100 (±1000)
AITKEN *et al.*[3]	70	0·042	74,500	42,900 (±1000)	40,400 (±1000)
Present work	80	0·0136	76,430	42,200 (±1200)	40,000 (±1200)
BIDINOSTI *et al.*[18]	120	0·018	80,500	42,200 (±1000)	39,700 (±1000)
Present work	130	0·0365	79,920	42,100 (±1200)	39,300 (±1200)
BIDINOSTI *et al.*[18]	137	0·0098	83,800	42,600 (±1000)	40,100 (±1000)
		Mean σ_0		42,300	40,000
		Value of σ_0 used for calculating g and s		42,030 [13]	39,900 [16]

conditions (Table 3). Different r values account for the apparent inversion of $\hat{\sigma}$ for 120° and 130°. Values of σ_0 calculated from equation (3) using the two independent sets of g and s values given by WESTCOTT [13] and PATTENDEN[16] are listed in Table 3. The constancy of σ_0, using any one set of g and s data is extremely good; this is particularly interesting, since cross-sections given by TATTERSALL *et al.*[17] and by AITKEN *et al.*[3] are based on "Harwell Standard Boron" (766·6 ± 3·5 barns), while

[16] N. J. PATTENDEN, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/11, United Nations (1959).

[17] R. B. TATTERSALL, W. A. COOPER, D. JOWITT and S. K. PATTENDEN, U.K.A.E.A. Report, AERE/R/R 2459 (1958).

the present work and that of BIDINOSTI *et al.*[18] is based on σ_0 for ^{59}Co being 36·6 and 36·5 barns respectively. It is clear that the reaction rate of ^{149}Sm in neutron spectra within the range covered by Table 3 is adequately accounted for by using an effective cross-section calculated from either set of g and s values. Integral cross-section measurements can throw no light on the accuracy of the two values of σ_0.

The integrated neutron flux was somewhat higher in experiment 3 (Table 1) and it was felt worthwhile to assay the ^{151}Sm content as described earlier. At this particular irradiation level the quantity of ^{151}Sm remaining is only very slightly dependent on the cross sections of both ^{149}Sm and ^{151}Sm; it is mainly dependent on the ^{150}Sm cross-section. By using the measured final atom ratio $151/150 = 0{\cdot}000250 \pm 0{\cdot}000005$, and taking $\hat{\sigma}$ for ^{149}Sm as 73,620 barns (Table 1) and $\hat{\sigma}$ for ^{151}Sm as 12,800 barns[18] the effective cross-section of ^{150}Sm in experiment 3 was found to be 102 ± 5 barns. The expression used for the calculation was based on the normal irradiation equations; it is too cumbersome to be quoted. It should be noted however, that a change of 10 per cent in the cross-sections of ^{149}Sm or ^{151}Sm leads to less than 1 per cent change in the calculated cross-section of ^{150}Sm.

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Acknowledgements—We wish to thank Mr. B. SLADE of the Isotopes Division, Harwell for the absolute standardization of cobalt sources and Dr. M. L. SMITH of the Electromagnetic Separator Group, Harwell, for supplying the enriched samarium. Thanks are also due to Mr. W. E. PERRY of the National Physical Laboratory, Teddington for recent data on the half-life of ^{60}Co, to Mr. D. JEFFERSON-LOVEDAY, Reactor Division, Harwell, for the measurement of moderator temperatures and Dr. H. ROSE of the Physics Division, Harwell, for advice and discussion.

[18] D. R. BIDINOSTI, H. R. FICKEL and R. H. TOMLINSON, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, A/Conf. 15/P/201. United Nations (1959).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 12 to 14. Pergamon Press Ltd.

THE α-HALF-LIVES OF ^{244}Cm, ^{245}Cm AND ^{246}Cm*

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(*Received* 21 *June* 1960; *in revised form* 1 *August* 1960)

Abstract—The α-half-life of ^{244}Cm, determined from specific activity measurements, and the α-half-lives of ^{245}Cm and ^{246}Cm, determined by mass spectrometric analysis of curium and its plutonium daughters, have been determined to be 17·59 ± 0·06 years, 9320 ± 280 years and 5480 ± 170 years, respectively.

IN long term high neutron flux irradiations of ^{239}Pu, both ^{242}Cm and ^{244}Cm are formed as shown in Fig. 1. As the plutonium is consumed by successive neutron capture or fission, the neutron capture–β-decay chain leading to ^{242}Cm is gradually terminated, and the ^{242}Cm present either decays or is transformed into heavier curium isotopes. Much of the presently available curium comes from samples of

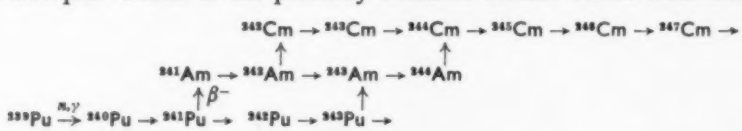

FIG. 1.

plutonium that have been exposed to a high neutron flux for a sufficient length of time that the chain leading to ^{242}Cm has been terminated, and the mass is made up principally of ^{244}Cm. Current chemical investigations,[1] require an accurate half-life value for the latter isotope, and this was determined in the present study by measurement of specific activity. Milligram amounts of pure $CmCl_3$ were weighed, then dissolved in a known weight of solution for radiometric assay.

Some of the presently available curium is sufficiently rich in ^{245}Cm and ^{246}Cm to enable a more accurate determination of the half-lives of these two isotopes than was possible earlier. The method used depends on the isotopic ratios of the plutonium daughters formed by α-decay of curium of known isotopic composition, using the newly determined value for the half-life of ^{244}Cm as a standard. These heavier curium isotopes are of particular interest to the chemist. As samples of curium are isolated in which the heavier isotopes constitute the principal fraction of the mass, the longer α-half-lives and thus lower specific activities associated with them will greatly decrease the health hazards and radiation effects involved in working with macro quantities of the element.

EXPERIMENTAL

The isolation of curium from samples of highly neutron irradiated ^{239}Pu has been discussed in several publications.[2,3] The curium as isolated was subjected to further chemistry to bring the

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

(1) W. T. CARNALL and P. R. FIELDS, *J. Amer. Chem. Soc.* **81**, 4445 (1959).
(2) W. C. BENTLEY, H. DIAMOND, P. R. FIELDS, A. M. FRIEDMAN, J. E. GINDLER, D. C. HESS, J. R. HUIZENGA, M. G. INGHRAM, A. H. JAFFEY, J. B. MAGNUSSON, W. M. MANNING, J. F. MECH, G. L. PYLE, R. SJOBLOM, C. M. STEVENS and M. H. STUDIER, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. p. 261. Vol. VII, United Nations, New York (1956).
(3) C. H. YOUNGQUIST and P. R. FIELDS, Supplement to the 1958 Nuclear Congress, Sixth Hot Laboratories and Equipment Conference, Chicago, Illinois (1958).

americium content of the sample below the detectable limit and separate the last traces of lanthanides. The americium–curium separation was accomplished by a series of oxidation cycles, each followed by precipitation with fluoride ion.[4] The lanthanide–curium separation was made using a cation exchange resin with 13 M HCl as the eluating agent.[5]

The upper limit of americium present in the final sample, set by spectrophotometric analysis of the curium solution, was 0·015 per cent. Alpha pulse height analysis showed that by activity, the sample was essentially pure ^{244}Cm. It contained less than 0·05% ^{242}Cm, and no other alpha emitters were detected. The isotopic composition of the curium sample used is given in Table 1. Spectrographic analysis of the curium indicated the presence of less than 1·5 per cent by weight of impurities, practically all of which was iron. The method of preparation of $CmCl_3$ gave a further opportunity to separate the sample from impurities, particularly iron, by fractional sublimation.

TABLE 1.—MASS SPECTROMETRIC ANALYSIS OF CURIUM
(^{244}Cm half-life determination)

Isotope	Mole %
^{244}Cm	94·57 ± 0·11
^{245}Cm	1·29 ± 0·04
^{246}Cm	4·14 ± 0·09

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The preparation of pure $CmCl_3$ with Cm_2O_3 as a starting material, using vacuum line techniques, has been discussed previously.[6] The method was applied to subliming pure $CmCl_3$ into a thin wall fused silica capillary tube which was subsequently sealed off the system. This capsule, containing approximately 3·5 mg $CmCl_3$, was weighed on an Ainsworth Model FDI microbalance, then split in two halves. The two halves of the capsule were repeatedly rinsed with dilute HNO_3, then dried and reweighed to determine net weight of $CmCl_3$. The washings were diluted to 50 ml with 0·4 M HNO_3; then 1 gm aliquots were weighed out and again diluted to 50 ml with 0·4 M HNO_3. Weighed aliquots of this latter solution were counted in a low geometry α-counter with a geometry factor ($1/G_p$) of 2111·6.[7,8] Suitable buoyancy corrections were applied to all weighings.[9] All samples were counted to less than 0·2 per cent error at the 0·01 level of confidence.

Plutonium daughters from a highly neutron irradiated sample of curium were periodically separated using an anion exchange column with HCl as eluant.[10] The plutonium was analysed mass spectrometrically. Six successive separations of plutonium at intervals of 3–4 weeks were made. To help insure that nonradiogenic plutonium present initially did not affect the results, twice during the course of these separations the curium was in addition subjected to an oxidation-fluoride precipitation cycle in an attempt to separate any residual plutonium. The ratio $^{241}Pu/^{240}Pu$ was constant throughout the successive separations; the $^{242}Pu/^{240}Pu$ ratio required two successive plutonium separations before reaching constancy. This was to be expected since the nonradiogenic plutonium in the sample was essentially all ^{242}Pu; less than 2 per cent of the original mass of plutonium remained at the end of the irradiation, and of this greater than 96 per cent was ^{242}Pu.

RESULTS AND DISCUSSION

The most recent investigation of the half-life of ^{244}Cm gave 18·4 years as the weighted average of two different experiments.[10] Of the two values averaged, 19·2 ± 0·6 and

[4] R. A. PENNEMAN and L. B. ASPREY, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. p. 355. United Nations, New York (1956).
[5] S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 6229 (1954).
[6] S. FRIED and W. H. ZACHARIASEN, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955. Vol.VII, p. 235. United Nations, New York (1956).
[7] A. H. JAFFEY, *The Actinide Elements* (Edited by G. T. SEABORG and J. J. KATZ) NNES. Plutonium Project Record, Vol. 4–14A, Chap. 16. McGraw-Hill, New York (1951).
[8] A. H. JAFFEY, *Rev. Sci. Instrum.* **25**, 349 (1954).
[9] *International Critical Tables*, Vol. 1, p. 71. McGraw-Hill, New York (1926).
[10] A. M. FRIEDMAN, A. L. HARKNESS, P. R. FIELDS, M. H. STUDIER, and J. R. HUIZENGA, *Phys. Rev.* **95**, 1501 (1954). (Note: Reference 1 in this paper should cite *Phys. Rev.* **94**, 974, (1954) instead of *Phys. Rev.* **94**, 1083 (1954).

17·9 ± 0·5 years, the former was based on the α-pulse and mass spectrometric analysis ($^{244}Cm/^{242}Cm$ ratio) of a curium sample assuming a known half-life of ^{242}Cm. The 17·9 year value depended entirely on mass spectrometric ratios together with the assumed half-life of ^{242}Cm. Alpha-pulse analysis is, in general, subject to greater errors than mass spectrometric results, and in this case the presence of a large α-per cent ^{242}Cm lent considerable uncertainty to the resolution of the lower energy ^{244}Cm peak. Thus the value 17·9 years is currently being used for the half-life instead of the averaged value.

The half-life of ^{244}Cm determined in the present study by specific activity measurements was 17·59 ± 0·06 years. This value is within the limits of error set by FRIEDMAN *et al.*, for their work.[10]

TABLE 2.—MASS SPECTROMETRIC ANALYSIS OF CURIUM AND DAUGHTER PLUTONIUM USED FOR ^{245}Cm AND ^{246}Cm HALF-LIFE DETERMINATION

Curium		Plutonium	
Isotope	Mole %	Isotope	Mole %
^{244}Cm	87·63 ± 0·13	^{240}Pu	99·9577 ± 0·0006
^{245}Cm	1·779 ± 0·024	^{241}Pu	0·00384 ± 0·0001
^{246}Cm	10·59 ± 0·13	^{242}Pu	0·0387 ± 0·001

Reported half-lives for ^{245}Cm vary between 7·5 ± 1·9 × 10^3 and 1·4 ± 0·3 × 10^4 years;[10,11,12] while those for ^{246}Cm vary between 2·3 ± 0·5 and 6·6 ± 0·3 × 10^3 years.[10,12,13,14] In the present investigation, expressions of the form given below (1),

$$t_{\frac{1}{2}}(^{245}Cm) = t_{\frac{1}{2}}(^{244}Cm) \times \frac{\text{mole \% } ^{245}Cm}{\text{mole \% } ^{244}Cm} \times \frac{\text{mole \% } ^{240}Pu}{\text{mole \% } ^{241}Pu} \qquad (1)$$

together with isotopic compositions given in Table 2, of which that for plutonium is typical of three runs, established the half-lives of ^{245}Cm and ^{246}Cm as 9320 ± 280 and 5480 ± 170 years respectively.

The errors quoted, except for α-counting, are based on standard deviation and arise principally from the mass spectrometric results.

[11] J. R. HUIZENGA and H. DIAMOND, *Phys. Rev.* **107**, 1087 (1957).
[12] C. I. BROWNE, D. C. HOFFMAN, W. T. CRANE, J. P. BALAGNA, G. H. HIGGINS, J. W. BARNES, R. W. HOFF, H. L. SMITH, J. P. MIZE and M. E. BUNKER, *J. Inorg. Nucl. Chem.* **1**, 254 (1955).
[13] J. P. BUTLER, T. A. EASTWOOD and H. G. JACKSON, *Phys. Rev.* **103**, 965 (1956).
[14] H. DIAMOND and R. BARNES, Argonne National Laboratory, report a value of 5·5 ± 1·0 × 10^3 years for the half-life of ^{246}Cm obtained by separating curium daughters from a sample of californium. This is the same method as described in reference 14. Private communication (1959).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 15 to 19. Pergamon Press Ltd.

THALLIUM ISOTOPES 192 AND 193

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(*Received* 28 *June* 1960)

Abstract—Half-lives of ^{192}Tl and ^{193}Tl have been determined by following the decay of conversion electron lines from mass separated sources in a β-spectrometer. From energy level systematics an (11·4 ± 1·4) min period is ascribed to a 7+ level in ^{192}Tl; most likely the ground state has the same half-life within the limits of error. Predicted M4 isomers in ^{192}Tl and ^{191}Tl could not be confirmed. The ground state half-life of the former isotope was obtained as (22·6 ± 1·0) min, while that of the latter seems to be less than 10 min. An improved half-life of ^{191}Au, (3·2 ± 0·1) hr, is reported.

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DATA concerning energy levels and decay properties of neutron deficient Tl isotopes down to $A = 194$ have been reported in a number of communications from this Institute.[1–6] These earlier investigations form the basis for the present continuation of the work towards lower mass numbers, partly by furnishing the experimental techniques and partly by revealing systematic trends, which could be used to predict certain features of the unknown decays.

Because of the short half-lives and complex level schemes to be expected in this low mass region, detailed spectroscopic studies were not primarily aimed at. Thus the principal result of the investigation, besides some contribution to the knowledge of level systematics, is the determination and assignment of half-lives. It must be emphasized, however, that rather powerful methods are needed even for this seemingly simple purpose when products of high energy nuclear reactions are dealt with. In many cases where conventional nuclear chemical techniques are likely to fail, the use of mass separated samples and energy resolving detectors as described in the following offers a way out of the difficulties.

1. EXPERIMENTAL PROCEDURES

Hg in the form of Hg_2Cl_2 was bombarded with 75–105 MeV protons in the Werner synchrocyclotron for 15–45 min. The target was dissolved in HNO_3 + HCl, most of the HNO_3 boiled off, and the solution adjusted to 6 N in HCl. After the addition of a few mg Tl carrier, the Tl ions were oxidized to Tl^{3+} with $KMnO_4$. $TlCl_3$ was separated from the target solution by ether extraction, and the organic phase containing the Tl was washed twice with 6 N HCl. A few drops of 6 N HCl were added and the ether evaporated, leaving $TlCl_3$ in the aqueous phase. After reduction to Tl^+ with H_2O_2 the solution was transferred to a small platinum crucible, fitting the ion source oven of our electro-magnetic mass separator[7,8] and evaporated to dryness.

The mass separation could normally start about 40 min after the irradiation. With a total ion current of 200–300 μA due to the stable carrier added, the cross section of the separated beams in the

[1] G. ANDERSON, E. ARBMAN and B. JUNG, *Ark. Fys.* **11**, 297 (1957).
[2] G. ANDERSSON, P. A. TOVE, B. JUNG and I. B. SVENSSON, *Nucl. Phys.* **3**, 493 (1957).
[3] G. ANDERSSON and I. BERGSTRÖM, *Nucl. Phys.* **3**, 506 (1957).
[4] G. ANDERSSON, J. O. BURGMAN and B. JUNG, *Phil. Mag.* **3**, 105 (1958).
[5] B. JUNG, *Nucl. Phys.* **10**, 440 (1959).
[6] B. JUNG and G. ANDERSSON, *Nucl. Phys.* **15**, 108 (1960).
[7] G. ANDERSSON, *Ark. Fys.* **12**, 331 (1957).
[8] J. O. BURGMAN and G. ANDERSSON, *Nucl. Instr.* **3**, 33 (1958).

focal plane (at 45° to the beam direction) had a half-width of 1·5–2 mm and a height of about 20 mm. The lines due to the stable Tl isotopes 203 and 205 as observed on a fluorescent screen were used to adjust the position of the spectrum in order to let the mass of actual interest reach a 2 mg/cm² Al strip, mounted on a β-spectrometer source holder and placed at a predetermined position behind a 1·5 mm wide slit. In this way nearly ideal sources for our two-directional focusing spectrometer[9] are obtained by direct deposition, that is, without further preparation.[10]

The amount of stable charge material added was chosen to correspond to a separation time of 10–30 min depending on the half-life studied, whereupon the source was transferred to the β-spectrometer. The automatic scanning device of this instrument was used to record repeatedly a limited energy region where conversion electron lines could be expected to appear. In a second run, the spectrometer was adjusted to accept a characteristic conversion line, the decay of which was followed down to the background at fixed spectrometer settings.

In calculating the half-lives, a weighted least squares treatment was applied. To the error thus obtained, another 2 per cent have been added, allowing for systematic errors. This is particularly intended to cover a possible change of the spectrometer magnetic field during the measurement, which is normally negligible, however.

2. THALLIUM-192

In the recent study of isomerism in even mass Tl isotopes[6] two facts were of particular importance in distinguishing between ground state and isomeric 7+ level. First, the high-spin level is not excited in the decays of the isobaric Pb isotopes, but can be produced by proton bombardment of Hg. Second, a characteristic low energy $E2$ transition appears only in the β-branches from the 7+ levels, while the similarly characteristic transition from the first excited state to ground state in Hg is fed also from the Tl ground states.

In the case of ^{192}Tl the preparation of pure ground state samples was considered unfeasible because of the expected short half-life of ^{192}Pb, already that of ^{194}Pb being only 11 min.[6] The energy systematics, however, gave a clear indication where to look for conversion lines from ^{192}Tl in the β-spectrometer (see Fig. 1).

With a ^{192}Tl sample prepared as described in Section 2, the prominent $L_{(II)}$ line of a 109 keV transition and the K and L lines of a (424 ± 1) keV $E2$ transition ($K/L \approx 2{\cdot}5$) were found, all showing an about 12 min period. The presence of the 109 keV transition, fitting nicely into the energy systematics (Fig. 1), makes it plausible to ascribe this half-life to an isomeric 7+ level. About the ground state nothing can be said with certainty. It may be short-lived enough not to show up at all, but a similar half-life to that of the isomer (cf. 33 min ^{194}Tl and 32·8 min ^{194m}Tl[6]) is not excluded by the present measurements. Both should then be contained within the error limits of our most accurate value, $(11{\cdot}4 \pm 1{\cdot}4)$ min, measured on K 424 in the β-spectrometer. This is in fact in accord with a recently observed systematic behaviour of beta half-lives far from stability[11] (see Fig. 3).

As to the series of low energy $E2$ transitions in the β-decays of isomeric 7+ states of Tl, it may be remarked that the assignments of the Hg levels involved are still unknown. The need for a detailed experimental study of the decay of at least one of the even mass Tl isomers, suitably 1·9 hr ^{198m}Tl is obvious.

3. THALLIUM-193

The energy systematics of some low-lying levels in odd mass Tl isotopes is shown in Fig. 2. Straight-line extrapolation to lower mass numbers indicates the possibility

[9] E. ARBMAN and N. SVARTHOLM, *Ark. Fys.* **10**, 1 (1956).
[10] J. KOCH (Editor), *Electromagnetic Isotope Separators and Applications of Electromagnetically Enriched Isotopes*, North-Holland Publishing Co. (1958).
[11] G. ANDERSSON, *Nucl. Phys.* in press.

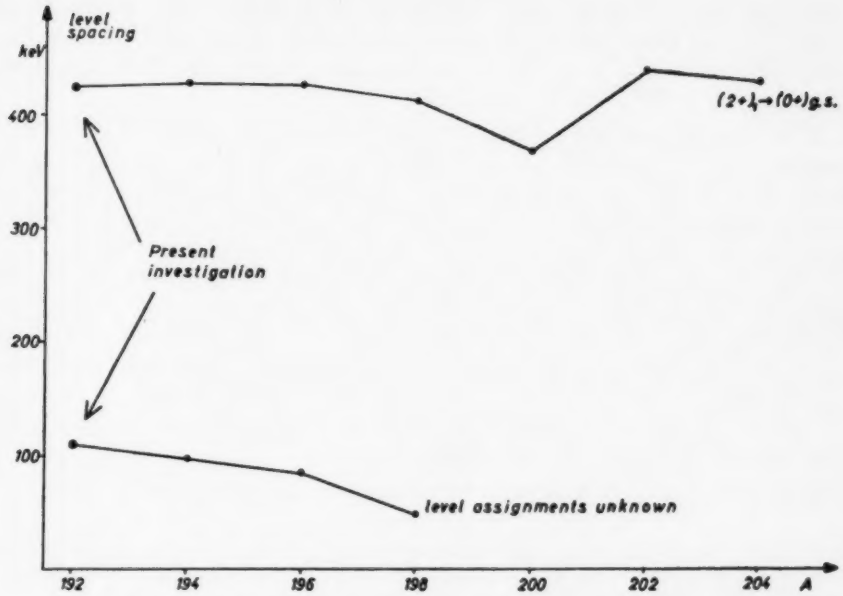

FIG. 1.—Variation with mass number of level spacings in even mass Hg isotopes. The upper curve is based on a series of strong $E2$ transitions present in the decays of both the ground states and the isomeric 7+ states of ^{195}Tl and lower even mass isotopes. The $E2$ transitions represented in the lower curve appear only in the decays of the 7+ states. (Data from ref. 6 and ref. 12.)

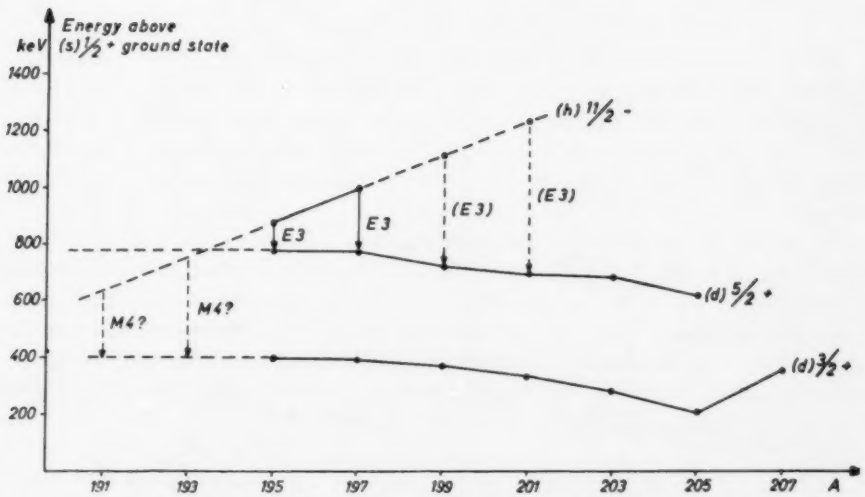

FIG. 2.—Variation with mass number of the excitation energy of some levels in odd mass Tl isotopes. (Data from ref. 12.)

that the $\frac{11}{2}-$ and $\frac{5}{2}+$ levels cross between $A = 195$ and $A = 193$, giving rise to relatively slow $M4$ transitions at $A \leq 193$ instead of the short-lived $E3$ transitions known to exist in ^{195}Tl (3·5 s), ^{197}Tl (0·55 s), and probably ^{199}Tl and ^{201}Tl (42 ms and 5 ms, respectively).[12]

In ^{193}Tl this rough systematics predicts an $M4$ transition of about 350 keV, which corresponds to a 45 min half-life if the matrix element of the transition is similar to that of other $M4$ transitions in the region.[13] A shorter half-life can be explained as caused by a β-branch from the isomeric state; this mode of decay receives increased importance towards highly neutron deficient nuclides (see for instance ref. 6).

The conversion electron spectrum of ^{193}Tl was found to contain a number of about 25 min lines in the energy region where $M4$ lines could be expected: E_{e-} (keV) = 241 (rel. intensity $\geqslant$ 100), 252 (~30), 261 (~25), 270 (~10), 291 (~3), 309 (~16), 321 (~7), and 330 (~4). It does not seem possible, however, to interpret any of these lines as belonging to an $M4$ transition. The half-life, (22·6 $\pm$ 1·0) min by measurement on the 309 keV line, would indicate a β-branch of about 50 per cent, which is not likely to prevent the highly converted internal transition from being detected in the conversion spectrum. This favours an assignment of the 23 min period to the ground state.

It is easily seen from the energy systematics (Fig. 2), that only minor deviations from linearity of the $\frac{11}{2}-$ and $\frac{5}{2}+$ curves are needed to retain $\frac{5}{2}+$ below $\frac{11}{2}-$ in ^{193}Tl. Further a 23 min half-life of the ground state fits well into the systematics shown in Fig. 3.

The (30 $\pm$ 3) min half-life assigned to ^{193}Tl by CHACKETT and CHACKETT[14] from ^{184}W (60 MeV N, 5n) studies does not agree altogether with our result. However, contributions from 33 min ^{194}Tl and 32·8 min ^{194m}Tl[6] cannot be excluded in their case.[15]

4. MASS NUMBER 191

Proceeding to ^{191}Tl in the extrapolated energy systematics (Fig. 2) we are led to the prediction of a 230 keV $M4$ transition. The half-life of the isomeric level in the absence of a beta branch would be about 2·5 hr. If the reported 10 min half-life of ^{191}Tl[14] were characteristic of this level, this would indicate almost 95 per cent β-decay, making the conversion lines of the hypothetical isomeric transition less prominent.

This may explain why no $M4$ transition was discovered in ^{191}Tl either. An alternative explanation is certainly that the $\frac{5}{2}+$ level is still below $\frac{11}{2}-$ or that some intervening level destroys the isomerism. As to the ground state, a 10 min period agrees with systematics (Fig. 3), but the conversion lines seen indicate a somewhat lower half-life. A satisfactory measurement has not been possible with the present technique of sample preparation. It may be suggested that an admixture of 11·4 min ^{192}Tl has contributed slightly to the reported half-life of ^{191}Tl, analogous to the case of ^{193}Tl–^{194}Tl.[15]

In the course of this investigation we found reason to study other members of the

[12] *Nuclear Data Sheets*. National Academy of Sciences—National Research Council, Washington, D.C (1958, 1959).
[13] I. BERGSTRÖM and G. ANDERSSON, *Ark. Fys.* **12**, 415 (1957).
[14] K. F. CHACKETT and G. A. CHACKETT, *J. Inorg. Nucl. Chem.* **13**, 1 (1960).
[15] K. F. CHACKETT, Private communication (1960).

191 mass chain. The earlier assignment of a 57 min half-life to ^{191}Hg[12] was mainly confirmed, although our preliminary value is markedly lower. This decay will be further studied together with those of other low mass Hg isotopes. The half-life of ^{191}Au was also checked and found to be (3·2 ± 0·1) hr by following the decay of an

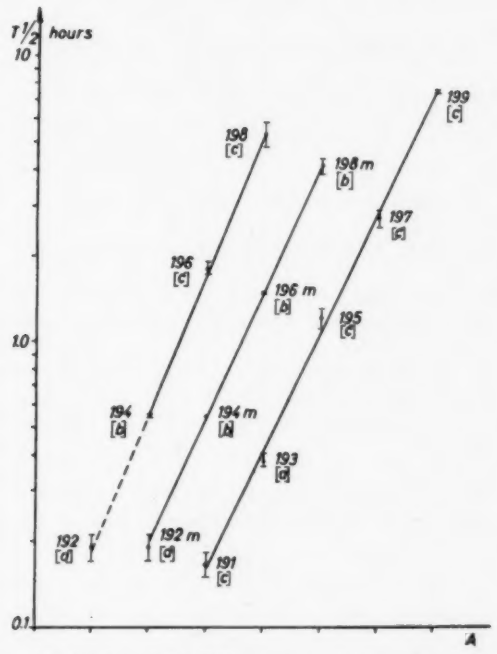

FIG. 3.—Semilogarithmic plot of β-half-lives versus mass number for neutron-deficient Tl isotopes. ^{195m}Tl and ^{196m}Tl have been corrected for internal branches; ^{194m}Tl and ^{192m}Tl are assumed to be ~100 per cent β-decaying. *a* = this work; *b* = ref. 6; *c* = ref. 12.

earlier unreported conversion line at 16·5 keV. The Hg samples used in these measurements were prepared from irradiated Au targets, which were put into the mass separator without preceding chemical separation. A more detailed description of this technique will be given elsewhere.[16]

Acknowledgement—We wish to express our gratitude to Professor T. SVEDBERG for the facilities put at our disposal and to Dr. K. CHACKETT for encouraging comments on our results. ING. Å. SVANHEDEN and the synchro-cyclotron crew have been cooperative as always and Mr. H. G. RIKNER has performed many of the mass separations.

[16] G. ANDERSSON and R. RINGH, *Ark. Fys.* **18**, 385 (1960).

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 20 to 25. Pergamon Press Ltd.

ASSOCIATED PROCESSES TO THE SZILARD–CHALMERS EFFECT IN CRYSTALS—I

HEXAMMINO-COBALTIC NITRATE

1. RADIATION ANNEALING OF THE CRYSTALLINE DEFECTS CONCOMITANT TO IRRADIATION IN THE REACTOR

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(*Received* 8 *April* 1960; *in revised form* 21 *July* 1960)

Abstract—The aim of the present paper is to study the annealing processes associated to the Szilard–Chalmers effect. By analogy with the annealing following the neutron irradiation, we may also take into account an annealing concomitant to the irradiation in the reactor. The annealing is described by means of the retention. It was observed that the retention increases with time until it reaches a saturation value R_∞, characteristic for a certain γ-dose-rate. This behaviour is rather difficult to interpret. There exists a great similarity between the obtained curves and the results usually found by heating the irradiated samples.

THE recombination of the fragments that appear as a result of the Szilard–Chalmers effect in crystalline compounds, is of no little interest for the study of kinetics of the chemical processes in crystals.

As a consequence of radiative neutron capture, the atom receives an amount of energy due to the photon emission. This amount can be large enough to break the chemical bound of the atom in the molecule. Thus by the breaking the initial molecule, we may find the radioactive recoil atom in another chemical form, which can be separated from the initial one. However, in most cases, a good deal of the activity is to be found in the initial chemical form. In accordance with the terminology introduced by LIBBY, we shall call retention,[1] the percentage of the activity which is retained in the initial chemical form.

At first sight, two possibilities which lead to retention appear. In the first place an inefficiency of the photon emission following the neutron capture may exist. In this way there is a probability that the compound nucleus may emit two or more photons, so that the total angular momentum may be zero, or, in any case, the energy transmitted to the atom may be lower than the chemical bond energy. The second process would consist of a substitution reaction of a hot atom. By analysing the above mentioned cases, we can see that the probability of these explanations leading to a substantial retention is small. The causes which lead to retention must therefore be of a different nature.

In order to elucidate the mechanism of retention we start from the following picture. As a result of thermal neutron capture in the crystalline lattices formed by molecules or molecular ions, the atoms which receive energies higher than the chemical bond energy will leave the nodes of the lattice. The atoms which do not suffer to

[1] W. F. LIBBY, *J. Amer. Chem. Soc.* **69**, 2523 (1947).

substitution reactions, i.e. the majority, will loose their kinetic energy by collisions with other atoms or the molecules of the lattice, or will simply be slowed down by the lattice field. In this way they will be distributed in the crystal at random. They will occupy position in the crystalline interstices and therefore they will be in a metastable state, which may last a very long time; this can be proved experimentally. By transfering energy to the system we may activate these interstitial atoms so that they will tend to reoccupy their initial positions of maximum stability, i.e. the lattice nodes.

The above mentioned effect has been demonstrated by WILLIAMS who irradiated the samples formerly irradiated with neutrons with ionizing radiation[2] and by GREEN and MADDOCK who heated the samples irradiated by neutrons.[3] It is remarkable that at a given temperature the retention reaches, after a long enough period, a saturation value that cannot be surpassed by further heating. The saturation value increases when the temperature is increased. On the other hand it has been proved that the retention is a function of the irradiation conditions.[4,5] By analogy with the radiation induced or thermally induced annealing following the irradiation by neutrons we may also expect radiation induced annealing, concomitant to the irradiation by neutrons. It is the purpose of the present paper to study the annealing processed associated to the Szilard–Chalmers effect.

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EXPERIMENTAL

Principles

The crystalline hexammino-cobaltic nitrate has been irradiated. For this compound, the Szilard–Chalmers effect has been studied only with a view to obtaining radiocobalt.[6] In this case, owing to the reaction $^{59}Co\ (n, \gamma)\ ^{60}Co$, the radiocobalt obtained leaves the complex $[Co(NH_6)_3]^{3+}$ ion in the form of a cobaltic ion Co^{3+}. By dissolving the irradiated sample in water, the unstable cobaltic ion passes into the cobaltous ion Co^{2+}. By an appropriate procedure, the two fractions may be separated chemically, and the retention established.

Irradiation

The samples, contained in quartz test-tubes, were irradiated in the thermal column of the I.F.A. reactor. The irradiation was carried out in air. Irradiation times ranged from 5 min to 40 hr.

The thermal neutron flux was determined through activation of copper foils, fast neutron flux through aluminium foils, and the γ-dose-rate was determined through chemical dosimetry with oxalic acid.

Separation

The procedure adopted was elaborated in the I.F.A. laboratories.[7] The irradiated sample was dissolved in distilled water, Pyridine and ammonium thiocyanate were added to the solution. By shaking up with chloroform, the pyridinic complex, was extracted containing the cobaltous fraction, while the cobaltic complexes remained in the solution. The two fractions were made up to equal volumes. Their activity was measured with a G.M. immersion counter, of the Vakutronik VA-Z type. Identical results were obtained for the same sample by using other separation methods such as: extraction with amyl alcohol and diethyl ether, isomyl alcohol, benzene etc but the first procedure was found to be the most efficient.

[2] R. WILLIAMS, *J. Phys. Coll. Chem.* **52**, 603 (1948).
[3] I. H. GREEN and A. G. MADDOCK, *Nature, Lond.* **164**, 788 (1949).
[4] M. M. DE MAINE, A. G. MADDOCK and K. TAÚGBØL, *Disc. Faraday Soc.* **23**, 211 (1957).
[5] N. SUTIN and R. W. DODSON, *J. Inorg. Nucl. Chem.* **6**, 91 (1958).
[6] G. KAYAS and P. SUE, *Bull. Soc. Chim. Fr.* 1145 (1950).
[7] S. IONESCU and C. GRIGORESCU-SABAU, *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1958, 15/P/1280. United Nations (1958).

Identification

A paper electrochromatographic identification of the products obtained by irradiation was tried using a well known technique.[8] Portions of 5–10λ of various concentrated solutions of the irradiated sample were put onto the zero line of a strip of Whatmann No. 1 paper. Dibasic ammonia citrate 0·01 M., chosen from a series of tested electrolytes, was used as supporting electrolyte. The potential gradient varied for different samples from 5 to 15 V/cm. The electromigrations lasted 1–6 hr. After the electromigration was stopped, the activity of the paper was measured, strip by strip, with a G.M. counter. The electrochromatograms of all samples studied presented only two peaks, independently

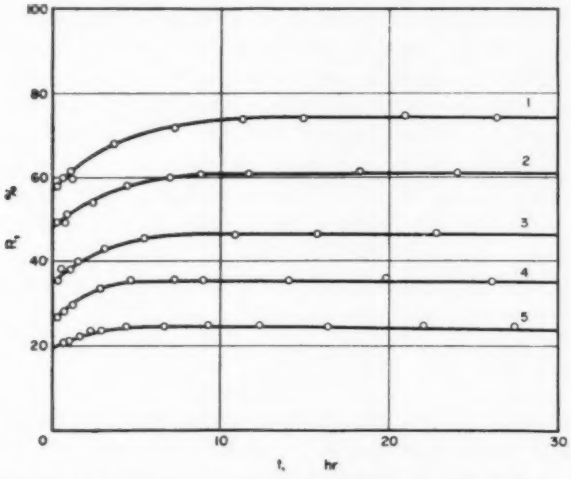

FIG. 1.—The variation of retention as a function of the irradiation time, in various conditions.

of the irradiation conditions. The identification of these two peaks was made by means of standard probes of hexammino-cobaltic nitrate and cobaltous nitrate, marked with ^{60}Co. By integrating the electrochromatogram, the value of the retention, obtained by extraction with solvents was found. In this way, the mechanisms which might lead to chemical species of the type $[Co(NH_3)_5NO_3]^{2+}$, $[Co(NH_3)_4(NO_3)_2]^{+}$, etc. have been excluded from the very beginning, these forms not having been found. A more detailed analysis, aimed at proving the existence of such chemical forms as $[Co(NH_3)_5H_2O]^{3+}$, $[Co(NH_3)_4(H_2O)_2]^{3+}$, etc. has not been made. Such forms might result from the depletion of the ammonia sextet coordinated to the cobalt, as a consequence of the processes, which took place during irradiation. Nevertheless, even if such forms existed, they would be contained in the hexammine fraction, and the mechanism of annealing would be the same.

RESULTS AND DISCUSSIONS

The retention of the samples irradiated in the thermal column under different conditions has been determined. It was observed that the retention increases with time, until it reaches a saturation value R_∞, characteristic for a certain γ-dose-rate. The greater the γ-dose-rate, the higher the values of R_∞. The experimental results are shown in Table 1. The values which were used represent the average of at least four measurements, the error being of $\pm 1{\cdot}5$ per cent.

It is apparent from Fig. 2 that R_∞ is proportional to the logarithm of the γ-dose-rate. The following experiments have been carried out to verify if R_∞ varies effectively with the γ-dose-rate. The samples irradiated in the reactor were subsequently submitted to irradiation from a ^{60}Co source. It was established that the samples which

[8] V. CROATTO, G. GIACOMELLO and A. G. MADDOCK, *Ric. Sci.* **21**, 1788 (1951).

TABLE 1.—CONDITIONS UNDER WHICH THE SAMPLES WERE IRRADIATED IN THE REACTOR

No. of the curve	The flux of thermal neutrons ϕ_t (cm^{-2} sec^{-1})	The flux of fast neutrons ϕ_f (cm^{-2} sec^{-1})	The γ-dose rate δ (rhr^{-1})	The saturation value of the retention R_∞ (%)	The initial retention R_0 (%)	The fraction destined to anneal $(\Delta R)_0$ (%)
1	$6{\cdot}0 \times 10^{11}$	$1{\cdot}75 \times 10^{11}$	$1{\cdot}31 \times 10^{7}$	74·5	57·1	17·4
2	$1{\cdot}2 \times 10^{11}$	$6{\cdot}25 \times 10^{9}$	$3{\cdot}47 \times 10^{6}$	61·1	48·4	12·7
3	$3{\cdot}0 \times 10^{10}$	$8{\cdot}75 \times 10^{9}$	$6{\cdot}55 \times 10^{5}$	46·6	36·0	10·6
4	$6{\cdot}0 \times 10^{9}$	$3{\cdot}12 \times 10^{8}$	$1{\cdot}73 \times 10^{5}$	35·1	26·5	8·6
5	$8{\cdot}8 \times 10^{8}$	$3{\cdot}10 \times 10^{5}$	$5{\cdot}36 \times 10^{4}$	24·5	19·0	5·5

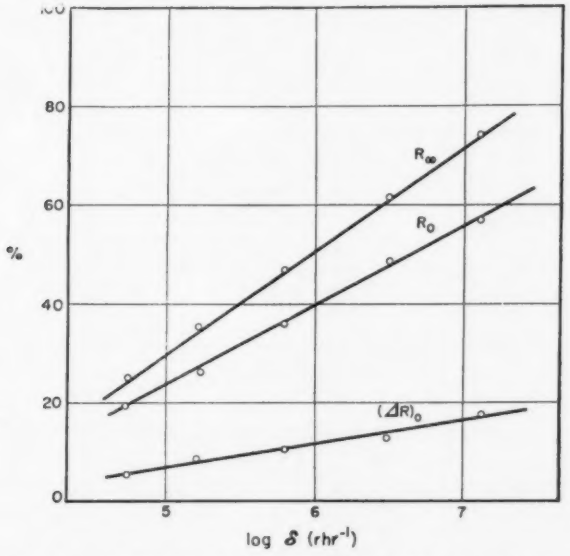

FIG. 2.—The variation of R_∞, R_0 and $(\Delta R)_0$ values with the γ-dose-rate.

TABLE 2.—THE RETENTION OF TWO SAMPLES AFTER THE γ-SOURCE IRRADIATION

The sample	The dose-rate in the reactor δ_R (rhr^{-1})	The dose in the reactor D_R (r)	The dose-rate the source δ_S (rhr^{-1})	The dose at the source D_S (r)	Retention in the reactor R_R (%)	Retention at the source R_S (%)
A	$6{\cdot}55 \times 10^{5}$	$6{\cdot}55 \times 10^{5}$	$1{\cdot}65 \times 10^{5}$	$1{\cdot}12 \times 10^{7}$	38·0	38·0
B	$5{\cdot}36 \times 10^{4}$	$1{\cdot}34 \times 10^{6}$	$1{\cdot}65 \times 10^{5}$	$1{\cdot}12 \times 10^{7}$	24·5	39·3

had been irradiated at a γ-dose-rate which was higher than that at the ^{60}Co source did not present any annealing. On the other hand, the sample irradiated in the reactor at a γ-dose-rate which was lower than that of the source, showed a remarkable annealing. The results are given in Table 2.

By studying the curves from Fig. 1 we can observe that at a given γ-dose-rate, after a relatively short period of irradiation, the retention becomes time independent. The existence of this time independence suggests the existence of an irreversible dynamic equilibrium which could characterise the annealing process. Thus, although new radioatoms are continually being formed, the ratio between the number of interstitial radioatoms and the number of atoms located at the nodes remains constant, independent of the period of irradiation.

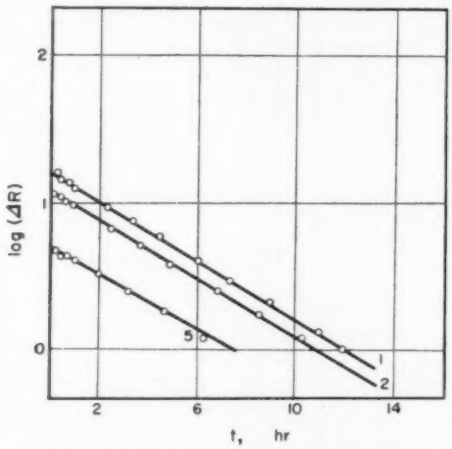

FIG. 3.—The decrease in time of the fraction which is destined to anneal for different γ-dose-rate.

It is possible to explore the decrease in the concentration of interstitial radioatoms which have yet to anneal, with the time, $\Delta R = R_\infty - R$. As a result of the analysis of the curves, it follows that there exist a first order process, characterized by rate constant k (Fig. 3). In fact, the equation of the annealing process can be written in the following way:

$$\Delta R = (\Delta R)_0 e^{-kt} \tag{1}$$

where $(\Delta R)_0 = R_\infty - R_0$, is the fraction destined to anneal in certain γ-dose-rate conditions. The R_0 value may be graphically determined from Fig. 3 and represents the initial retention of the sample. Values of R_0 and $(\Delta R)_0$ are given in Table 1.

In Fig. 3 we also notice that the rate constant k is the same for all irradiated samples whatever the irradiation conditions, and is equal to $3{\cdot}1 \times 10^{-5}$ sec^{-1}. The values R_∞, R_0 respectively $(\Delta R)_0$ are the only ones which varies from one sample to another, being a function of the irradiation conditions. These variations satisfied the relations.

$$R_\infty = a_\infty \log \delta/\delta_0 \tag{2}$$

$$R_0 = a_0 \log \delta/\delta_0 \tag{3}$$

$$(\Delta R)_0 = a \log \delta/\delta_0 \tag{4}$$

where δ_0 is the value of the γ-dose-rate corresponding to $R_\infty = 0$. From Fig. 2 it follows that $\delta_0 = 3{\cdot}75 \times 10^3$ rhr^{-1}.

As has been shown above, R_∞ does not depend on the dose, but on the dose-rate. This behaviour is rather difficult to interpret.

There exists a considerable similarity between the curves obtained (Fig. 1) and the results usually found on heating the irradiated samples. The fraction which is destined to anneal increases with increase in the dose-rate in the same way as a greater number of interstitial atoms anneal if the temperature is increased. It has not yet been possible to reach a definite conclusion, about theoretical basis of this experimental evidence.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 26 to 30. Pergamon Press Ltd.

GAMMA-INDUCED REACTIONS BETWEEN BORON HALIDES AND HYDROGEN

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(*Received* 20 *May* 1960; *in revised form* 30 *August* 1960)

Abstract—This paper reports the results of a study directed toward the preparation of diborane by a γ-induced reaction between boron halides and hydrogen. As we will show, diborane is not formed either as a product or intermediate; instead, the irradiation of BCl_3–H_2 or BBr_3–H_2 mixtures induces the formation of HX and a white, stable polymer of the general formula $(BX_2)_n$ where X refers to the respective halogen.

ALTHOUGH there is no published work directly pertinent to this study, the work of SCHLESINGER and BURG[1] and of URRY *et al.*[2] indicate that the formation of diborane might be induced in a radiation field. SCHLESINGER and BURG, for example, obtained diborane in low yield by passing a mixture of H_2 and BCl_3 through a 15,000 V discharge.

URRY *et al.* improvement on previous preparations of B_2Cl_4 in liquid[3] and gaseous discharges[4] might also suggest B_2Cl_4 would be formed as an intermediate in the radiation field and then further converted to form B_2H_6 according to the following equilibrium:

$$B_2Cl_4 + H_2 \rightleftharpoons H_2B_2Cl_4 \rightleftharpoons BCl_3 + B_2H_6$$

A recent communication by SCHAEFFER and ROSS reports on the photolytic formation of diborane from SiH_4 and BCl_3.[5] The photolytic reaction in this instance was induced in the presence of methyl radicals resulting from the photolytic decomposition of azomethane. The significance of their study lies in the evidence of the directing influence of a chain initiator on a reaction which is thermodynamically permissible but which does not proceed in this direction under normal conditions.

In a study similar to that reported here ROSENBERG and WARTIK[6] report on reactions of BCl_3 and BBr_3 in an ozonizer-type discharge with CO, CO_2, SO_2, and N_2. The BCl_3–CO system is of most interest to the present study since one might expect to form B_2Cl_4 via the reaction

$$2BCl_3 + CO \rightarrow B_2Cl_4 + COCl_2.$$

Although traces of phosgene were formed, no B_2Cl_4 was produced. The major product was a nonvolatile film of a 1-1 B-Cl polymer.

[1] H. I. SCHLESINGER and A. B. BURG, *J. Amer. Chem. Soc.* **53**, 4321 (1931).
[2] G. URRY, T. WARTIK, R. E. MOORE and H. I. SCHLESINGER, *J. Amer. Chem. Soc.*, **76**, 5293 (1954).
[3] A. STOCK, A. BRANDT, H. FISCHER, *Ber. Dtsch. Chem. Ges.* **58**, 855 (1925).
[4] T. WARTIK, R. E. MOORE and H. I. SCHLESINGER, *J. Amer. Chem. Soc.* **71**, 3265 (1949).
[5] R. SCHAEFFER and L. ROSS, *J. Amer. Chem. Soc.* **81**, 3486 (1959).
[6] R. M. ROSENBERG and T. WARTIK. The Pennsylvania State University, Pennsylvania (1958) (ASTIA Document No. 206769).

EXPERIMENTAL

Mixtures of BCl_3 or BBr_3 and H_2 were made up in a standard high-vacuum system and sealed off in Pyrex vessels for irradiations. The reaction vessels were approximately 4 in. diameter by 8 in. long (approximately 1 litre volume) and contained a break-seal for reopening the vessel on the vacuum line after irradiation.

Irradiations were carried out in Battelle's cobalt-60 facility. This facility contains approximately 2200 c. The dose rate used in this study varied between approximately 2 and 3×10^5 rep/hr depending on the source configuration used. Dose rates were determined by means of standard ferrous sulphate dosimetry.

After irradiation the vessel was reattached to the vacuum system and gases were separated by standard fractional condensation techniques. Hydrogen was measured with the aid of a Toepler pump. Other gases were measured volumetrically and analysed from vapour-pressure and infra-red data.

RESULTS

Prior to embarking on a series of irradiations it was necessary to determine the general stability of diborane in a radiation field. A vial containing diborane was therefore exposed to a γ-dose of 10^8 rep at a dose rate of 2×10^5 rep/hr and at an average ambient pool temperature of 15 C. Since diborane is not completely stable at this temperature a nonirradiated control sample was also maintained at the same temperature. The irradiated sample exhibited about 1·4 per cent decomposition due to radiation after subtracting the thermal blank obtained from the control sample. This calculated to a G-value of approximately seven molecules per 100 eV for the radiation-induced decomposition of diborane, a surprisingly low value considering the thermal instability of diborane.

Following this encouraging result five irradiations and one thermal reaction were carried out as listed in Table 1. Runs 2A and 4A are so designated because they are reactions of polymer, formed in Runs 2 and 4, respectively, with hydrogen. Run 2A was a thermal reaction, carried out at pool temperature and Run 4A was an irradiation reaction. The G-values (molecular yields) are calculated for the formation of HX, that is, HCl or HBr. The yields reported are over-all yields, based on the amount of HX formed over the entire radiation period. Comparable G-values for the consumption of boron halide are readily obtained from the ratio

$$\frac{\text{HX formed}}{\text{BX}_3 \text{ consumed}} = \frac{G_{\text{HX}}}{G_{-\text{BX}_3}}$$

DISCUSSION OF RESULTS

The four irradiations of BX_3–H_2 mixtures show rather clearly that the over-all stoicheiometry is

$$2BX_3 + H_2 \rightarrow 2HX + (BX_2)_n.$$

The data are too limited to establish a complete curve of HX formation (or BX_3 depletion) against dose. It appears that the reaction does not approach any steady state condition, but instead goes to completion. This conclusion is also supported by the fact that in a preliminary experiment a BCl_3–H_2 mixture received a dose of 10^8 reps, and yielded only HCl and H_2 as volatile products; all the BCl_3 had been consumed—apparently converted to BCl_2-polymer. Run 4A shows that a back-reaction between H_2 and polymer is extremely slight at ambient temperature. A comparable back-reaction between HCl and polymer was not investigated, but it is reasonably certain that this too would not occur.

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TABLE 1.—γ-INDUCED REACTIONS BETWEEN BORON HALIDES AND HYDROGEN

Run No.	Dose rate (10^{-5} rep/hr)	Time (hr)	Total dose, (10^{-5} rep)	Pool temp, (C)	Reactants (mmoles)			Products (mmoles)			Reactants consumed (mmoles)		G_{HX}, (molecules/ 100 eV)
						BX_3	H_2	BX_3	H_2	HX	BX_3	H_2	
1	3·10	0·32	0·98	9	BCl_3	6·26	16·2	4·44	15·3	1·63	1·82	0·9	23000
2	3·06	1·22	3·72	9	BCl_3	7·71	24·0	4·66	23·7	3·13	3·05	0·3	9100
2A	—	144	—	20	—	—	9·15	—	7·07	1·6	—	2·08	—
3	2·55	1·37	3·48	9	BBr_3	1·02	3·51	0·46	3·21	0·68	0·56	0·30	7600
4	2·15	2·00	4·30	25	BBr_3*	6·01	17·8	5·30	17·2	1·00	0·71	0·6	2390†
4A	2·15	4·65	10·0	25	—	—	4·72	—	4·46	0·04	—	0·26	—

* BBr_3 present as liquid and gas (approx. 65 per cent gas).
† G_{HX} (vapour phase calc) 2390
G_{HX} (vapour + liquid) 1550

The high *G*-values are characteristic of systems in which H and Cl atoms and HCl are present. Such systems are capable of propagating extremely long chains. Ordinarily one does not obtain as long chains with Br atoms. Although the introduction of bromine in these systems in the form of BBr_3 appears to have reduced the *G*-values markedly, the values are still high. This would indicate that the radical chain may not be related to a hydrogen-halogen atom chain but to another process. The ionization potential for H_2 being 15·4 eV and that of BCl_3^+ and BCl_2^+ being 12·0 and 13·2 respectively,[7] it would appear that H_2^+ would transfer charge to BCl_3 so that the primary step in these systems would involve chain initiation through the boron halide. Since no steady state condition is reached, termination reactions such as $H + H = H_2$ and $BX_2 + X = BCl_3$ are excluded. A probable mechanism is as follows

BX_3	$\rightsquigarrow BX_2 + X$	(1)	Initiation
$X + H_2$	$\longrightarrow HX + H$	(2)	
$H + BX_3$	$\longrightarrow HX + BX_3$	(3)	
$BX_2 + BX_3$	$\longrightarrow (BX_2)_2 + X$	(4A)	Propagation
$(BX_2)_{n'} + BX_3$	$\longrightarrow (BX_2)_{n''} + X$	(4B)	
$(BX_2)_{n'} + BX_2$	$\longrightarrow (BX_2)_n$	(5)	

Based on the stoicheiometry obtained in this study Steps 4A and 4B do not occur with the frequency of the other steps. Along with Step 1 however Steps 4A and 4B probably account for the propagation of the reaction via halogen atom formation. The intermediates BX_2 and $(BX_2)_2$ in Steps 3 and 4A are not to be identified with B_2Cl_4. As discussed earlier, if such were the case diborane would have been produced in these reactions. The steps proposed here also support the fact that the reaction does not reach a steady-state condition, but instead goes to completion as the H_2 or BX_3 are consumed.

The $(BX_2)_n$ polymer reported here has a number of interesting properties:

(1) The polymer is a white, sublimable solid, and is not attacked by dilute HCl or boiling NaOH. (The authors use the term "polymer" in this paper with some hesitation. Inasmuch as a molecular weight was not obtained and the polymer is sublimable, the value of n for $(BX_2)_n$ is probably not large.)

(2) The polymer is the first to be reported where the halogen-boron ratio is greater than one.

(3) The polymer is stable in a radiation field.

(4) The polymer contains no boron–boron bonds and is therefore presumed to be composed only of boron-halogen bonds. (The boron–boron bonds in boron halides such as B_2Cl_4 or B_4Cl_4 are readily broken by reaction with water, acid, or base.)

The 2:1 ratio of halogen-to-boron in the polymer is not based on direct analysis of the polymer. However, the stoichiometry obtained from the analysis of volatile components indicates such a ratio as a minimum ratio.

The 2:1 ratio make the polymer "analogous" elementally to B_2Cl_4. This analogy may also be compared with the polymer obtained by ROSENBERG and WARTIK[6] where a 1:1 halogen–boron polymer was produced "analogous" to B_4Cl_4. In both instances however the analogies must be restricted to the elemental ratios only. B_2Cl_4 and

[7] F. H. FIELD and J. L. FRANKLIN, *Electron Impact Phenomena*. Academic Press, New York (1957).

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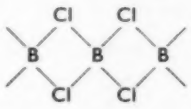
B_4Cl_4 are relatively unstable compounds, contain B–B bonds, and react with hydrogen to yield diborane. The polymers formed in these studies possess none of these characteristics.

On heating the evacuated, irradiated reaction vessel containing only the polymer, the polymer sublimed to cold portions of the line with no apparent decomposition; that is, no condensible gases were trapped in the vacuum system during this operation.

The $(BX_2)_n$ polymer was completely stable in acid or base. Upon reacting the polymer with hydrogen (Runs 2A, thermal; and 4A, irradiation) only traces of HCl were obtained, with no sign of diborane or other boron hydride. Based on these results it is hypothesized that the polymer consists of long chains, possibly interlocking chains, of bridge-type B—Cl—B bonds in the manner



CONCLUSIONS

The fact that diborane has been prepared in gaseous discharges of BCl_3–H_2 mixtures under some conditions indicates that the inability to prepare B_2H_6 or B_2Cl_4 in an irradiation field may be related to the lack of the proper chain-directing species in the reaction mechanism. In instances where diborane has been prepared such as in STOCK's[3] and SCHLESINGER's[1] investigations, metal vapours were also present in the discharge. Likewise in the photolytic reaction of SCHAEFFER and ROSS[5] it is apparent that a chain-directing species (the methyl radicals from the azomethane) is responsible for the path of the reaction.

The incompletely identified BX_2-polymer described in this study warrants further investigation.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 31 to 42. Pergamon Press Ltd.

THE CHEMICAL EFFECTS OF NEUTRON CAPTURE IN *CIS*- AND *TRANS*-DICHLOROBIS–(ETHYLENE-DIAMINE)–COBALT(III) NITRATE*

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(*Received* 23 *May* 1960)

Abstract—The kinetics of the isothermal annealing of ^{60}Co(5·3 years) and ^{38}Cl(37·5 min) recoil species in *cis*- and *trans*-$[Co(en)_2Cl_2]NO_3$ have been investigated. After a given isomer was irradiated, neither ^{60}Co nor ^{38}Cl was found in any appreciable amount in the other isomeric form, nor did any appear as the other isomer upon annealing. Average energies of activation of 5 kcal/mole and 6·5 kcal/mole were found for the ^{60}Co and the ^{38}Cl annealing processes, respectively, which correspond to entropies of activation of -61 cal °C^{-1} mole^{-1} and -56 cal °C^{-1} mole^{-1}. The increase in the retention of ^{60}Co and ^{38}Cl is described in terms of competitive reactions in the recoil sites. The increase in the retention due to isothermal-annealing processes occurring during the lifetime of the hot zone was estimated, and was found to be negligible.

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NEUTRON irradiation of solid compounds produces radioactivity in chemical forms which are often capable of undergoing further reaction when the target compounds are heated after irradiation. These so-called *isothermal-annealing* reactions, which have become an important aspect of the hot-atom chemistry of solids, have recently been studied in several complex compounds of cobalt.[1–4] The nature of the metastable recoil species and the kinetics of their annealing reactions are not entirely understood, and the extent to which reactions take place during the rapid slowing-down of the recoil atoms is not clear.

The present work is the extension of a preliminary study,[5] and is concerned with the isothermal annealing of ^{60}Co and ^{38}Cl recoil species in *cis*- and *trans*-$[Co(en)_2Cl_2]NO_3$. Several kinetic models are considered, and a model based on the competitive annealing reactions of the fragments in a given recoil site is found to account for several features of this as well as several previous investigations. An estimate is made which indicates that the extent to which the thermal-annealing reactions take place during the slowing-down of the recoil atom is quite small.

EXPERIMENTAL

Preparation of compounds. Quantities of *cis*- and *trans*-$[Co(en)_2Cl_2]Cl$ were prepared according to BAILAR.[6] The nitrate salts were precipitated by adding ammonium nitrate to a chilled solution of

* Research performed under the auspices of the U.S. Atomic Energy Commission.

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‡ Department of Chemistry, Brookhaven National Laboratory, Upton, New York.

§ Departments of Chemistry, Brookhaven National Laboratory, Upton, New York and Columbia University, New York.

(1) A. ZUBER. Thesis, Columbia University, New York (1954). USAEC Document NYO–6142 BNL.
(2) H. RAUSCHER and G. HARBOTTLE, *J. Inorg. Nucl. Chem.* **4**, 155 (1957).
(3) A. NATH, K. S. VENKATESWARLU and J. SHANKAR, *Proc. Indian Acad. Sci.*, **46** A, 29 (1957).
(4) A. NATH, S. B. SRIVISTAVA, *J. Inorg. Nucl. Chem.* **7**, 143 (1958).
(5) H. RAUSCHER, N. SUTIN and J. M. MILLER, *J. Inorg. Nucl. Chem.* **12**, 378 (1960).
(6) J. C. BAILAR, *Inorganic Syntheses* (Edited by W. C. FERNELIUS) Vol. 2, p. 223. McGraw-Hill, New York (1946).

the chlorides, and were purified by recrystallization. A single batch of each of the purified nitrates was used for the experiments in this study.

Irradiation and annealing conditions. Samples were irradiated at −78°C in fused silica ampoules which had been sealed under reduced pressure. All samples were irradiated at a neutron flux of $1{\cdot}1 \times 10^{13}$ neutrons cm^{-2} sec^{-1}, a cadmium ratio of 38, and a γ-ray flux of approximately 1×10^7 r hr^{-1}. The samples in which the ^{60}Co species were studied were irradiated for 5 min and stored in dry-ice for several days before annealing. Those samples in the ^{38}Cl study which were to be annealed for less than 1 hr were irradiated for 15 sec, while those samples which were to be annealed for 1, 2 and 4 hr were irradiated for 30 sec, 1 min and 2 min respectively. The samples were annealed at $61{\cdot}5 \pm 0{\cdot}2$°C by immersion in boiling chloroform, and at $80{\cdot}0 \pm 0{\cdot}1$°C and $100{\cdot}0 \pm 0{\cdot}1$°C by immersion in a constant temperature bath.

Chemical procedures. The percentage of the ^{60}Co present as Co^{2+}, or as forms exchangeable with Co^{2+}, was determined by solvent extraction. The sample was dissolved in a solution buffered at pH 7 which contained Co^{2+} carrier. This solution was extracted with chloroform that contained one per cent 8-hydroxyquinoline, the organic and aqueous phases were diluted to known volumes, and aliquots of each phase were counted.[7]

The percentage of the ^{38}Cl present as Cl^-, or as forms exchangeable with Cl^-, was determined by an ion-exchange method. An aliquot of an aqueous stock solution of the irradiated sample was passed through a Dowex-50 cation-exchange column. Since the radioactivity in the effluent decayed with the half-life of ^{38}Cl, it may be concluded that all the radioactive cobalt was retained on the column. The ion-exchange separation was performed as rapidly as possible, and the stock solution and the resin column were chilled in ice in order to reduce the extent of aquation of the complex ions.[8] A second aliquot of the stock solution was treated with H_2S to decompose the complex ions and to precipitate ^{60}Co as CoS. An aliquot of the filtrate from this precipitation was counted to obtain a measure of the total ^{38}Cl in the stock solution. This counting rate was compared with that of a sample of the effluent from the Dowex-50 column to obtain the percentage of the total ^{38}Cl present as radioactive Cl^-.

The percentage of the radioactivity in the parent form, the *retention*, was determined by a specific activity method. (It was shown earlier that after the irradiation of a given isomer, less than one per cent of the total activity of ^{60}Co as well as ^{38}Cl was found in the other isomeric form, for both annealed and unannealed samples.[5]) For the measurement of the ^{60}Co retention, a stock solution was prepared which contained the annealed compound and carrier of the same isomer. The absorbancy of the stock solution was measured with a Beckman model DU spectrophotometer at 618 mμ for *trans* and at 535 mμ for *cis* samples. A portion of the stock solution of a given irradiated isomer was added to a carrier solution of the other isomer. An aliquot of this mixed stock solution was counted, and sodium perchlorate was added to the remainder to precipitate *trans*-$[Co(en)_2Cl_2]ClO_4$. In the event of a *trans* target, the perchlorate salt was dissolved in water and *trans*-$[Co(en)_2Cl_2]NO_3$ was precipitated with ammonium nitrate. The nitrate salt was redissolved in water and purified by repeated precipitation. For *cis* targets, the perchlorate salt was discarded, and ammonium nitrate was added to the remaining solution which was then chilled to precipitate *cis*-$[Co(en)_2Cl_2]NO_3$. The nitrate salt was again purified by several reprecipitations. The retention was computed from the absorbancy and the counting rate of a solution of a given purified nitrate fraction from the appropriate absorbancy and counting rate of the mixed stock solution.

The procedures for measuring the retentions of ^{38}Cl were the same as those for ^{60}Co, with the modification that each aliquot taken for counting was first treated with H_2S to separate the cobalt from the chlorine.

A portion of the ^{60}Co and the ^{38}Cl was unaccounted for in each analysis. This unidentified activity was probably in the form of a complex ion closely related to the parent species.

Counting procedures. All samples were counted as liquids, in a well-type NaI(Tl) scintillation counter. Counting rates were corrected for decay and coincidence losses. The deviations of duplicate samples from a particular analysis were usually greater than the statistical counting errors.

RESULTS

The values of the retention as the parent form, the percentage of the activity as the

[7] T. MOELLER, *Industr. Engng. Chem., Anal. Educ.* **15**, 346 (1943).
[8] R. G. PEARSON, P. M. HENRY and F. BASOLO, *J. Amer. Chem. Soc.* **79**, 5379 (1957).

other isomer, and the percentages of the free and of the unidentified activities are shown in Table 1. It is interesting to note that a negligible amount of the ^{60}Co and the ^{38}Cl appears in the *trans* form when the *cis* compound is irradiated, and vice versa. The changes in the retention and of the free activity as a function of the annealing

TABLE 1.—DISTRIBUTIONS OF ^{60}Co AND ^{38}Cl

Chemical form	Annealing treatment	*cis* ^{60}Co	*trans* ^{60}Co	*cis* ^{38}Cl	*trans* ^{38}Cl
R*	none	3·1 ± 0·1	7·3 ± 0·5	12·5 ± 0·1	15·5 ± 0·4
R′*	none	0·1	0·2	0·4	0·7
F†	none	88·9 ± 0·3	82·3 ± 0·4	82·1 ± 0·9	79·8 ± 1·6
U‡	none	7·0 ± 0·3	10·2 ± 0·6	5·0 ± 0·9	4·0 ± 1·6
R	1 hr at 100°C	42·9 ± 1·3	48·0 ± 2·1	67·9 ± 1·2	70·1 ± 1·3
R′	1 hr at 100°C	0·1	0·1	0·3	0·4
F	1 hr at 100°C	45·3 ± 2·2	41·5 ± 4·4	30·4 ± 0·1	28·5 ± 0·3
U	1 hr at 100°C	11·7 ± 2·5	10·4 ± 4·9	1·4 ± 1·2	1·0 ± 1·3

* R—Retention, R′—percent of the total activity as the other isomer
† F—Free Activity, $\%^{60}Co$ as Co^{++} or $\%^{38}Cl$ as Cl^-
‡ U—Unidentified activity

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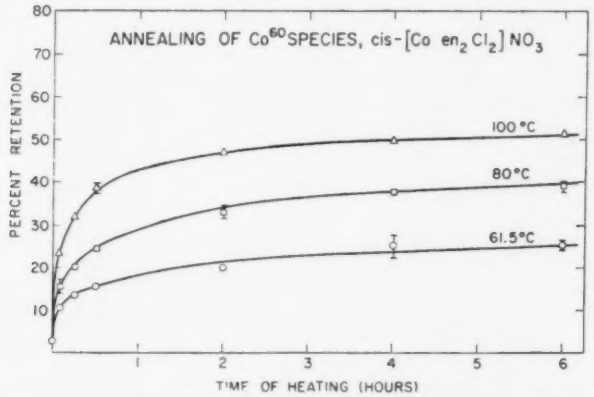

FIG. 1.—Annealing of ^{60}Co species, *cis*-$[Co(en)_2Cl_2]NO_3$ Per cent retention vs. time of heating (hr).

conditions are shown in Fig. 1–8. The errors indicated in the figures are the deviations of duplicate results from their averages. The limiting percentages of the activity in each form for each annealing curve were estimated by extrapolation. These limiting values, referred to as plateau values and designated with the subscript (∞), and the initial values for the unannealed samples are given in Table 2.

DISCUSSION

The rate of annealing of ^{60}Co and ^{38}Cl recoil species into a given parent form, as measured by the change in the retention, was followed at three temperatures. Fig. 1, 3, 5 and 7 indicate that the retentions rise to plateau values which appear to depend on the annealing temperature. This type of behaviour, which seems to be general in

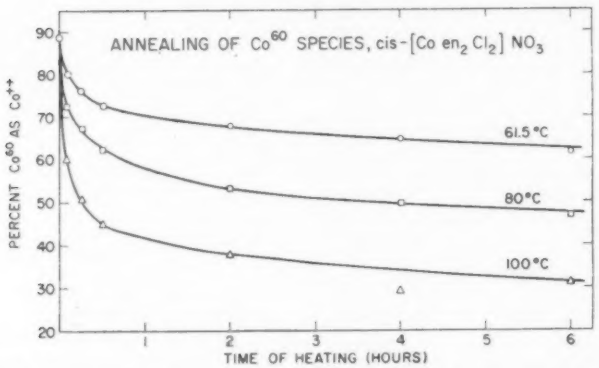

FIG. 2.—Annealing of ^{60}Co species, *cis*-$[Co(en)_2Cl_2]NO_3$ Per cent ^{60}Co as Co^{2+} vs. time of heating (hr).

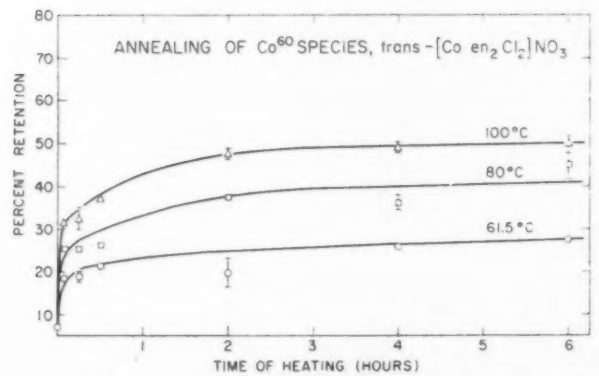

FIG. 3.—Annealing of ^{60}Co species, *trans*-$[Co(en)_2Cl_2]NO_3$ Per cent retention vs. time of heating (hr).

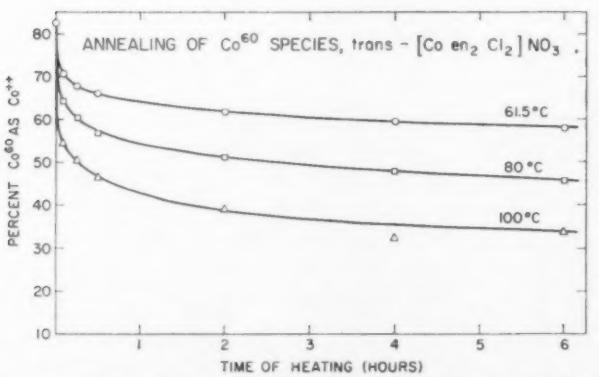

FIG. 4.—Annealing of ^{60}Co species, *trans*-$[Co(en)_2Cl_2]NO_3$ Per cent ^{60}Co as Co^{2+} vs. time of heating (hr).

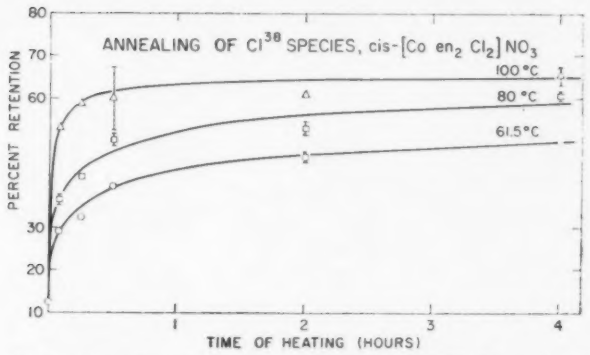

FIG. 5.—Annealing of ^{38}Cl species, *cis*-$[Co(en)_2Cl_2]NO_3$ Per cent retention vs time of heating (hr).

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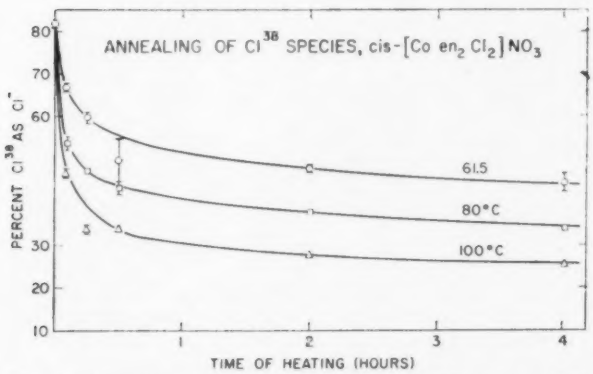

FIG. 6.—Annealing of ^{38}Cl species, *cis*-$[Co(en)_2Cl_2]NO_3$ Per cent ^{38}Cl as Cl^- vs. time of heating (hr).

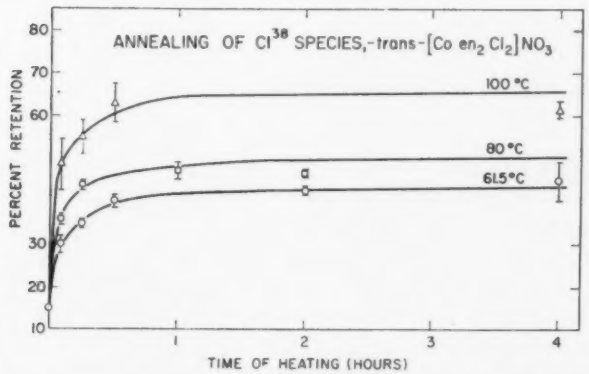

FIG. 7.—Annealing of ^{38}Cl species, *trans*-$[Co(en)_2Cl_2]NO_3$ Per cent retention vs. time of heating (hr).

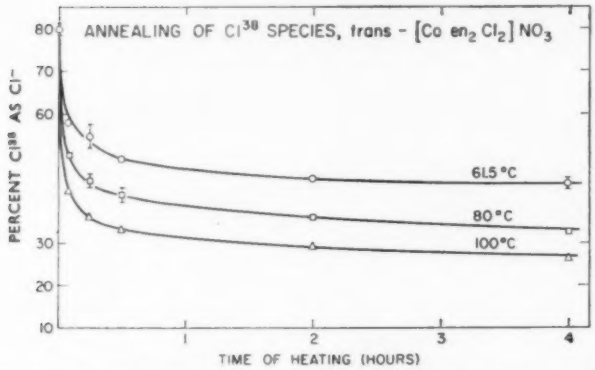

FIG. 8.—Annealing of ^{38}Cl species, *trans*-$[Co(en)_2Cl_2]NO_3$ Per cent ^{38}Cl as Cl^- vs. time of heating (hr).

TABLE 2.—INITIAL AND PLATEAU DISTRIBUTION OF ^{60}Co AND ^{38}Cl IN ANNEALED *cis*- AND *trans*-$[Co(en)_2Cl_2]NO_3$

Chemical form	Annealing temperature (°C)	*cis* ^{60}Co	*trans* ^{60}Co	*cis* ^{38}Cl	*trans* ^{38}Cl
R_0*	—	3·1 ± 0·1	7·3 ± 0·5	12·5 ± 0·1	15·5 ± 0·4
R_∞	61·5	26 ± 1	29 ± 2	51 ± 2	44 ± 2
R_∞	80·0	41 ± 2	41 ± 2	60 ± 2	50 ± 2
R_∞	100	52 ± 1	50 ± 1	65 ± 1	66 ± 2
F_0†	—	88·9 ± 0·3	82·2 ± 0·4	82·1 ± 0·9	79·8 ± 1·6
F_∞	61·5	60 ± 1	57 ± 1	44 ± 2	43 ± 2
F_∞	80·0	45 ± 1	45 ± 1	43 ± 2	32 ± 2
F_∞	100	30 ± 1	33 ± 2	24 ± 2	25 ± 2
U_0‡	—	8 ± 3	10·5 ± 2	5·4 ± 0·9	4·7 ± 1·5
U_∞	61·5	13 ± 1	15 ± 1	8 ± 2	12 ± 1
U_∞	80·0	14 ± 1	15 ± 3	8 ± 3	15 ± 3
U_∞	100	17 ± 2	20 ± 2	10 ± 2	13 ± 2

* R—Retention
† F—Free Activity, $\%^{60}Co$ as Co^{++} or $\%^{38}Cl$ as Cl^-
‡ U—Unidentified activity

recoil-atom annealing studies, has been observed in tris-acetylacetone cobalt(III),[3] α-tris-glycine cobalt(III),[4] and in oxyanion salts, such as potassium bromate,[9] potassium chromate,[10] and sodium arsenate.[11]

Because of the shorter times of annealing in the present study as compared to the work cited above, it is possible that on continued annealing the retentions might approach a common value, and the conclusion that there are plateaus which depend on the annealing temperature might be premature. In potassium chromate, for example, prolonged heating increased the retention of ^{51}Cr to nearly 100 per cent,[10]

[9] J. W. COBBLE and G. E. BOYD, *J. Amer. Chem. Soc.* **74**, 1282 (1952).
[10] A. G. MADDOCK and M. M. de MAINE, *Canad. J. Chem.* **34**, 275 (1956).
[11] H. KAWAHARA and G. HARBOTTLE, *J. Inorg. Nucl. Chem.* **9**, 240 (1959).

but such has not been the case for any of the cobalt complexes studied. There are thus two different approaches in treating the annealing data in recoil-atom studies. The first assumes a single temperature-independent plateau value of the retention, while the second assumes temperature-dependent plateaus. The data in this study will be considered from both points of view.

Temperature-independent plateau. If there is a temperature-independent plateau, and the approach to it were governed by a single activation energy, the phenomenological method of PARKINS *et al.*[12] for determining the activation energy for defect annealing can be applied. This method does not require a knowledge of the rate constants or the order of reaction, provided that some physical property monotonically related to the number of defects can be measured as a function of time, relative to a given initial value for all samples annealed.

If these conditions are met, the activation energy is given by

$$t \exp(-E/RT) = \text{constant}, \tag{1}$$

where t is the time required at the temperature T to reach a given value of the physical property. The activation energy is obtained from a plot of log t vs. T^{-1}, which should give a straight line with a slope that is independent of the value of the physical property that is chosen.

HARBOTTLE and SUTIN[13] have pointed out that for recoil atom annealing studies, the quantity $(R_\infty - R)$ can be regarded as linearly proportional to the total number of annealable defects, if a recoil atom not in the parent form is regarded as an annealable defect. If R_∞ is independent of temperature, annealing at various temperatures to a given value of the retention would be equivalent to a constant value of $(R_\infty - R)$ and the conditions for equation (1) would be met.

The data for Figs. 1, 3, 5 and 7 were plotted on an expanded scale and the times required at the three temperatures to reach a given value of R were determined, for at least ten values of R. The appropriate times were obtained from smoothed curves drawn through the experimental points, rather than directly from the original data. Log t was plotted vs. T^{-1} for each value of R, the best straight line was drawn through the points, and the energy of activation was computed from the slope. A family of lines with increasing slopes, corresponding to a wide range of activation energies, was obtained for each annealing reaction, rather than lines with a constant slope and a constant energy of activation. The apparent energies of activation for the annealing of ^{60}Co and ^{38}Cl ranged from 10 to 40 kcal/mole.

These results clearly show that the annealing process in each of the four cases studied can not be described by a single activation energy. Since it is not possible on the basis of these results alone to determine whether more than one process, each with a single activation energy, a single process with a spectrum of activation energies or some alternative scheme is responsible for the above behaviour, the results do not show conclusively that the assumption of a constant value of R_∞ is incorrect.

Temperature-dependent plateaus. Further information about the annealing processes was obtained by assuming first-order kinetics and plotting log $(R_\infty - R)$ *vs* time, using the temperature-dependent values of R_∞ at the three annealing temperatures as listed in Table 2. ZUBER[1] made such plots for the annealing of ^{60}Co in $[Co(en)_3]$

[12] W. E. PARKINS, G. J. DIENES and F. W. BROWN, *J. Appl. Phys.* **22**, 1012 (1951).
[13] G. HARBOTTLE and N. SUTIN, *Advances in Inorganic and Radiochemistry* (Edited by H. J. EMELÉUS and A. G. SHARP) Vol. 1, pp. 268–314. Academic Press, New York (1959).

$(NO_3)_3$, and obtained curves resolvable into two straight lines that were interpreted in terms of two first-order reactions. The annealing of ^{60}Co in α-tris-glycine cobalt(III)[4] was similarly attributed to three or more first-order reactions.

The data for all four annealing reactions in this study, when plotted as described above, gave curves which were resolved into two straight lines. An example of this plot, for the annealing of ^{60}Co in *trans*-$[Co(en)_2Cl_2]NO_3$ at 61·5°C, is shown in Fig. 9. The intercepts (I) and the first-order rate constants (k) obtained from the slopes of the lines are shown in Table 3, where the subscript (1) refers to the steeper of the two lines.

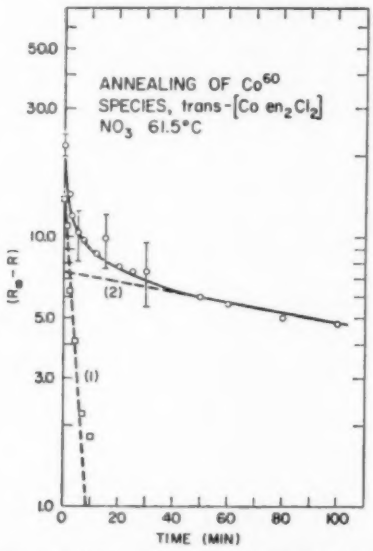

FIG. 9.—Annealing of ^{60}Co species, *trans*-$[Co(en)_2Cl_2]NO_3$ 61·5°C, $(R_\infty - R)$ vs. time of heating (hr).

No errors are quoted since these rate constants depend strongly on the smoothed curves drawn through the experimental points. Their orders of magnitude and temperature dependence, however, are qualitatively reliable.

The rate constants in Table 3 were plotted against T^{-1} to obtain apparent activation energies for the annealing reactions. The activation energy for the annealing of ^{60}Co in the *cis* and *trans* compounds averaged about 5 kcal/mole, while that for the annealing of ^{38}Cl was about 6·5 kcal/mole. Entropies of activation were calculated from the following equation for the rate constant:

$$k = (RT)/(Nh) \exp(\Delta S^*/R) \exp[(-E_a/RT) + 1], \quad (2)$$

where R is the gas constant per mole, N is Avogadro's number and h is Planck's constant. The average entropy of activation at 100°C for the annealing of ^{60}Co was -61 cal °C^{-1} mole^{-1} while that for the annealing of ^{38}Cl was -56 cal °C^{-1} mole^{-1}.

The relatively low energies of activation may reflect the availability of recoil energy, stored in the form of disorder, for driving the annealing reaction. Similarly the relatively high negative entropies of activation may be understood in terms of the increased order associated with the annealing processes.

The intercepts in Table 3 are seen to be temperature dependent; a result that has also been obtained in previous analyses of this type. MADDOCK and de MAINE[10] and HARBOTTLE and SUTIN[13] have pointed out that temperature-dependent intercepts are inconsistent with several kinds of recoil sites in which each kind of site contains a recoil atom that is annealable by a first-order process to give labelled parent only. If such were the case, the intercepts of the straight lines from plots of log $(R_\infty - R)$ vs. t would be temperature independent and proportional to the initial number of each kind

TABLE 3.—RATE CONSTANTS AND INTERCEPTS FROM PLOTS OF LOG $(R_\infty - R)$ VS. TIME

Annealing reaction	T (°C)	I_1 $(R_\infty - R)_0$	I_2 $(R_\infty - R)_0$	k_2 ($sec^{-1} \times 10^4$)	k_1 ($sec^{-1} \times 10^5$)
^{60}Co annealing in *cis*-$[Co(en)_2Cl_2]NO_3$	100	25·5	21·5	3·8	4·6
	80·0	20·5	16·5	1·4	4·3
	61·5	12·5	10·4	0·91	4·0
^{60}Co annealing in *trans*-$[Co(en)_2Cl_2]NO_3$	100	18·5	24·2	2·2	9·1
	80·0	15·0	18·7	1·8	8·8
	61·5	7·5	13·7	0·77	6·2
^{38}Cl annealing in *cis*-$[Co(en)_2Cl_2]NO_3$	100	10·4	42·1	5·9	11·2
	80·0	23·2	23·0	4·9	7·2
	61·5	17·2	21·3	2·1	3·9
^{38}Cl annealing in *trans*-$[Co(en)_2Cl_2]NO_3$	100	15·7	30·0	6·0	11·3
	80·0	9·2	20·0	4·6	7·1
	61·5	11·0	17·5	4·0	2·7

of defect. Temperature-dependent plateaus and temperature-dependent intercepts may be explained, however, in terms of competitive annealing processes.

The possibility of a metastable radioactive fragment subject to competitive reactions, one of which could lead to the parent, has been previously considered.[10,3] Such processes can be formulated more generally, however, in terms of a recoil site containing a radioactive atom and all of the molecular fragments produced in the slowing-down of the recoil atom. The species within a given recoil site would be subject to competitive reactions, which could lead to a variety of products, not all of which are radioactive. Simplified kinetics result if the number of possible products is limited, and if it is assumed that the defect sites are annealed with over-all first-order kinetics. If only one kind of recoil site is present, the following reactions might be considered:

$$\xrightarrow{k_1} p^* + f_1$$

$$s \xrightarrow{k_2} x^* + f_2$$

$$\xrightarrow{k_3} r^* + f_3$$

where s is the recoil site, p^* is the labelled parent molecule, x^* is a second labelled molecule, and r^* is an unco-ordinated recoil atom which may diffuse through the solid and perhaps undergo further reactions. The symbols f_1, f_2, and f_3 refer to the fragments which remain when the corresponding labelled entities are formed from the recoil site.

The recoil sites will be annealed according to the rate expression

$$dS/dt = -(k_1 + k_2 + k_3)S, \tag{3}$$

where S is the number of recoil sites. Integration of equation (3) gives

$$S = S_0 \exp [-(k_1 + k_2 + k_3)t], \tag{4}$$

where S_0 is the number of recoil sites at the beginning of the annealing.

The labelled parent is produced according to the rate expression

$$dP^*/dt = k_1 S = k_1 S_0 \exp [-(k_1 + k_2 + k_3)t], \tag{5}$$

where P^* is the number of labelled parent molecules. An expression for the retention may be obtained by integrating of equation (5), recalling that

$$R = \frac{(100)P^*}{N} \tag{6}$$

where N is the number of radioactive atoms present. The plateau value of the retention is obtained at t equal to infinity, which gives

$$R_\infty = R_0 + \frac{k_1 S_0'}{k_1 + k_2 + k_3}, \tag{7}$$

where S_0' is the percentage of the radioactivity present in the recoil sites at the start of the annealing, and R_0 is the initial value of the retention. If the rate constants are expressed in the form

$$k_i = A_i \exp (-E_i/RT), \tag{8}$$

the temperature dependence of R_∞ is readily explained in terms of the different energies of activation for the several reaction paths.

An expression for $(R_\infty - R)$ may be obtained from equations (5) and (6), and is equal to

$$(R_\infty - R) = \frac{k_1 S_0'}{k_1 + k_2 + k_3} \exp [-(k_1 + k_2 + k_3)t]. \tag{9}$$

Plots of log $(R_\infty - R)$ vs. t at various annealing temperatures should be straight lines with temperature-dependent intercepts, but the logarithms of the apparent rate constants obtained from the lines should not give a straight line when plotted against T^{-1}. It is interesting to note that the annealing data for tris-acetylacetone cobalt(III) have these characteristics.[3]

Two or more kinds of recoil sites seem to be necessary for the discussion of other annealing data. A scheme such as

$$\begin{array}{ll} \xrightarrow{k_1} p^* + f_1 & \xrightarrow{k_4} p^* + f_4 \\ S_1 \xrightarrow{k_2} x^* + f_2 & S_2 \xrightarrow{k_5} x^* + f_5 \\ \xrightarrow{k_3} r^* + f_3 & \xrightarrow{k_6} r^* + f_6 \end{array}$$

leads to the following expressions for R_∞ and $(R_\infty - R)$:

$$R_\infty = R_0 + \frac{k_1 S'_{01}}{k_1 + k_2 + k_3} + \frac{k_4 S'_{02}}{k_4 + k_5 + k_6} \tag{10}$$

$$(R_\infty - R) = \frac{k_1 S'_{01}}{k_1 + k_2 + k_3} \exp\left[-(k_1 + k_2 + k_3)t\right] + \frac{k_4 S'_{02}}{k_4 + k_5 + k_6} \exp\left[-(k_4 + k_5 + k_6)t\right], \tag{11}$$

where S'_{01} and S'_{02} are the percentages of the radioactivity present as each of the two kinds of recoil sites at the start of the annealing.

A temperature-dependent value of R_∞ for each kind of recoil site is, of course, again obtained. Plots of log $(R_\infty - R)$ vs. t should be resolvable into two straight lines, each with temperature-dependent intercepts. The data in Table 3 seem to be accounted for by this type of model. Since the rate constants obtained would be a sum of rate constants, it would not be possible to obtain the individual energies of activation from plots of log k vs. T^{-1} without considerably more data. The annealing of ^{60}Co in α-tris-glycine cobalt(III) requires several kinds of recoil sites, since the plots of log $(R_\infty - R)$ vs. t indicated the presence of three or more straight lines.[4]

The models outlined above are simplifications. For example, the production of labelled parent by diffusion-controlled reactions of the species r^* was neglected. The kinetics of models with additional kinds of recoil sites, and with multiple reaction paths for a given kind, could be readily derived, but severe requirements would be placed on the precision and the quantity of the data needed to determine the number of recoil sites and the number and energies of activation of the reaction paths for a given kind of site.

Preservation of configuration. As mentioned earlier, when a given isomer is irradiated, no appreciable activity appears in the other isomeric form either before or after annealing. This observation, together with the low energies of activation and the high negative entropies of activation for the annealing reactions, are consistent with the interpretation of the annealing phenomena as an ordering process. This ordering may be thought of as analogous to a recrystallization, with the crystalline phase surrounding the recoil site acting as a template from which the annealing may proceed, leading to the formation of the parent isomeric form only.

Reactions during the lifetime of the hot zone. The extent and duration of the excitation produced by recoil atoms in solids has been considered by SEITZ and KOHLER[14], who found that an atomic interchange process with a frequency factor (ν_0) of the order of 10^{13} or 10^{14} sec^{-1} and an energy of activation of 1 eV, had a reasonable chance of taking place during the cooling of the recoil-produced hot zone. HARBOTTLE and SUTIN[15] have extended the concept of the hot zone to systems of interest in hot-atom chemistry, and have pointed out that because of the entropy of activation, the formation of a complex chemical species might be less probable than an atomic interchange process.

It was of interest to make an order-of-magnitude calculation of ΔR, the increase in retention due to thermal annealing reactions during the lifetime of the hot zone. A simple expression for R was chosen,

$$dR/dt = kS', \tag{12}$$

and it was assumed that S' is approximately constant and equal to 100 per cent, and

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that k can be expressed as

$$k = A \exp(-E/RT). \tag{13}$$

The value of ΔR is then equal to

$$\Delta R = \int_{t_1}^{t_2} (dR/dt)\, dt = (100)A \int_{t}^{t_2} \exp(-E/RT)\, dt. \tag{14}$$

The expression for the temperature of the material surrounding the recoil atom as a function of time, used by SEITZ and KOHLER[14] was

$$T = \frac{Q}{8\pi^{3/2} cd(Dt)^{3/2}} \tag{15}$$

or $T = Kt^{-3/2}$, where Q is the heat deposited by recoil, c is the heat capacity, d is the density, and D is the thermal diffusivity.

For the purposes of integrating equation (14), the constants in equation (15) were assumed to be temperature independent. To avoid considering the decomposition of parent species formed during the hot zone, an upper limit corresponding to a temperature of 573°K (200°C) was arbitrarily chosen. The lower limit corresponded to 0°K. Parameters appropriate to an isothermal annealing reaction were chosen. A value of k equal to 5×10^{-3} sec^{-1} at 373°K and an energy of activation of 5 kcal/mole, gave a value of A equal to 4·4 sec^{-1}. The general expression for ΔR was then

$$\Delta R = \frac{(100)AK^{2/3}}{(E/R)^{3/3}} \int_{u=4\cdot4}^{u=0} u^{-1/3} \exp(-u)\, du. \tag{16}$$

where $u = (E/RT)$.

Estimates were made of the constants contained in K. The value of the integral, which is an incomplete gamma function, was about 1×10^{-2}, and the product of the terms to the left of the integral was about 2×10^{-8}, which gave a value for ΔR of the order of 10^{-1}. The factors that effect the magnitude of ΔR to the greatest extent are the upper limit of the temperature and the frequency factor A. If the complication of decomposition were neglected and higher values of the initial temperature were allowed, the value of the integral would approach a value of about one, which would give a value of ΔR of the order of 10^{-8}. Both of these values of ΔR are negligible, a result which is due primarily to the large negative entropy of activation for the annealing process, confirming the expectations of HARBOTTLE and SUTIN.[15]

It is reasonable to assume in view of these results that thermal annealing processes, with kinetic parameters similar to those chosen in this calculation, do not take place to any appreciable extent during the cooling of the hot zones. The processes responsible for the initial values of the retention must have entropies or energies of activation which are substantially different from those of the annealing reactions. Nevertheless, both classes of reactions show the same steric behaviour with respect to the exclusive production of a specific isomer. The pre-annealing reactions could occur either during the lifetime of the hot zone or at the ambient temperature of the target material following irradiation.

Acknowledgement—One of us (H. E. R.) is grateful to Brookhaven National Laboratory for an appointment as a Junior Research Associate, and to the National Science Foundation for the receipt of a Fellowship during the academic year 1955–1956.

[14] F. SEITZ and J. S. KOEHLER, *Solid State Physics* (Edited by F. SEITZ and D. TURNBULL) Vol. 2, pp. 305–448. Academic Press, New York (1956).

[15] G. HARBOTTLE and N. SUTIN, *J. Phys. Chem.* **62**, 1344 (1958).

J. Inorg. Nucl Chem. 1961, Vol. 17, pp. 43 to 54. Pergamon Press Ltd.

ELECTRONEGATIVITIES OF NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

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(*Received* 8 *September* 1960)

Abstract—The relative electronegativities of the Group VB elements in the trivalent state have been determined by methods based on thermochemical data and nuclear magnetic resonance and have the values 3·04 for nitrogen, 2·19 for phosphorus, 2·18 for arsenic, 2·06 for antimony and 2·16 for bismuth. Chemical and physical properties, including nuclear quadrupole resonance, ionization potentials, enthalpy of formation of halides and oxides, electrical and thermal conductivity, oxidation potentials, and the preparation and stability of pentahalides are correlated with these electronegativity values. Electronegativity values obtained by other methods are discussed.

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AN INVESTIGATION of the electronegativities of carbon, silicon, germanium, tin and lead by several physical techniques suggested the decreasing order of electronegativities, carbon > lead > germanium > tin > silicon, for these elements in sp^3 valence states.[1] This order is explainable in terms of the transition metal contraction and the lanthanide contraction and is consistent with many chemical and physical observations. The relative electronegativities of the neighbouring group, nitrogen, phosphorus, arsenic, antimony and bismuth are evaluated herein by the best available methods.

THE THERMOCHEMICAL SCALES OF ELECTRONEGATIVITY

The scale of electronegativity[2,3] based on the difference between the bond energy E(A—B) and the average of the bond energies E(A—A) and E(B—B) was re-evaluated[4] in 1960 using the most recent thermochemical data. The scale was also revised by HAISSINSKY[5] in 1946, by HUGGINS[6] in 1953, and by PAULING[7] in 1960. The results are presented in Table 1. As indicated in Table 1, data for nitrogen and bismuth are sparse.

TABLE 1.—ELECTRONEGATIVITY VALUES FROM CHEMICAL DATA

	N	P	As	Sb	Bi
PAULING (1939)	3·0	2·1	2·0	1·8	—
(1960)	3·0	2·1	2·0	1·9	1·9
HAISSINSKY (M^{III})	3·0	2·1	2·0	1·8	1·8
(M^{V})			2·2	2·1	>2·3
HUGGINS	3·05	2·15	2·10	2·05	—
ALLRED (Ref. 4)	3·04	2·19	2·18	2·05	2·02
Computations in Ref. (4)	2	5	5	4	1

[1] A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 269 (1958).
[2] L. PAULING, *J. Amer. Chem. Soc.* **54**, 3570 (1932).
[3] L. PAULING, *Nature of the Chemical Bond*, Chap. 2. Cornell University Press, Ithaca. (1939).
[4] A. L. ALLRED (Submitted to *J. Inorg. Nucl. Chem.* for publication). In Press *J. Inorg. Nucl. Chem.*
[5] M. HAISSINSKY, *J. Phys. Radium.* **7**, 7 (1946).
[6] M. L. HUGGINS, *J. Amer. Chem. Soc.* **75**, 4123 (1953).
[7] L. PAULING, *Nature of the Chemical Bond*, (3rd Ed.) p. 93. Cornell University Press, Ithaca (1960)

The re-evaluation in Ref. (4) indicates that phosphorus has approximately the same electronegativity as arsenic and that the value for trivalent bismuth is higher than previous values. The variation of electronegativity with period number appears to be monotonic here instead of alternating as in Group IVB.[1]

ELECTRONEGATIVITIES FROM NUCLEAR MAGNETIC RESONANCE (NMR)

The chemical shift of NMR depends upon several factors, one of which is the extent of diamagnetic shielding of a nucleus by the electrons in close proximity. If other factors are kept constant and groups with increasing electron-attracting ability

TABLE 2.—ELECTRONEGATIVITY VALUES FROM CHEMICAL SHIFT DATA

	N	P	As	Sb	Bi
100% $(CH_3)_3M$ (p.p.m.)	3·22	4·15	4·15	4·06	3·40
0% $(CH_3)_3M$ (p.p.m.)	3·18	4·30	4·39	4·53	4·19
Electronegativity	(3.04)	(2·19)	2·17	2·07	2·31

are successively substituted near the nucleus being observed by NMR, the extent of shielding of that nucleus is decreased and resonance occurs at a lower magnetic field with a constant frequency. The proton resonance conditions for the methyl halides are shown in Fig. 1[8] as a function of electronegativity.[4] The chemical shifts are for infinitely dilute solutions of the methyl halides in carbon tetrachloride, and the proton resonance of water is the external reference $[\delta = (H_s - H_{ref})/H_{ref} \times 10^6]$. Thus, NMR can be employed to obtain relative electronegativities of elements in carefully selected analogous compounds.

Experimental. In this research the chemical shifts of the trimethyl derivatives of the Group VB elements were observed and employed in the determination of relative electronegativities.

Trimethylamine, Eastman reagent grade, was distilled twice, and the fraction boiling at 3·5°C was used. Trimethylphosphine was prepared by the reaction of methylmagnesium iodide in n-butyl ether with phosphorus trichloride. During the addition and two hours afterwards, the reactants were stirred and immersed in a Dry-Ice-acetone bath. Then the reaction mixture was stirred for 4 hr at 0°C and for 6 hr at 25°C. The trimethylphosphine was distilled twice through a thirty-plate distillation column, and the fraction with a b.p. of 42°C was retained. An analysis by mass spectrometry showed the product to be >99·9 per cent trimethylphosphine. Trimethylarsine (b.p. 53°C) and trimethylstibine (b.p. 80·6°C) were made by the method described for trimethylphosphine. Trimethylbismuthine was prepared by reacting solid bismuth trichloride with methylmagnesium iodide in diethyl ether for 12 hr at room temperature and then at reflux temperature for 2 hr. The trimethylbismuthine was purified by high vacuum techniques. The product had a b.p. of 108°C and a proton magnetic resonance spectrum consisting of a single peak.

Each 5 mm o.d. Pyrex sample tube contained a sealed glass capillary filled with water, a trimethyl derivative, and enough 2,2-dimethylpropane to give a concentration of 5, 10, 25, 50, 75, and 100 per cent trimethyl derivative by volume. The height of the solution in the sample tube was approximately 10 cm.

The chemical shifts presented in Table 2 and Fig. 2 were measured with a Varian Associates V-4300B high resolution NMR spectrometer, equipped with a flux stabilizer and air turbine sample spinner, at 40 MC/s and 25°C. The chemical shifts between the protons in the methyl groups and the protons of water were measured by the side-band technique and are reported in parts per million $[\delta \text{ (p.p.m.)} = (H_s - H_T)/H_T \times 10^6]$. The accuracy is about ±0·01 p.p.m. In a few cases, the NMR

[8] A. L. ALLRED and E. G. ROCHOW, *J. Amer. Chem. Soc.* **79**, 5361 (1957).

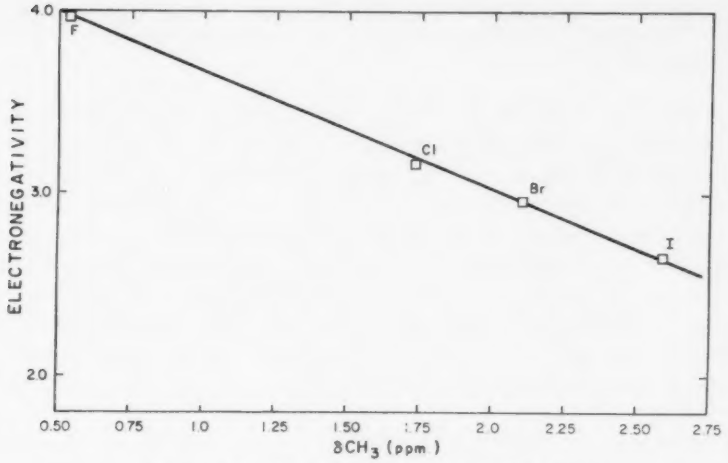

FIG. 1.—Chemical shifts of protons in methyl halides

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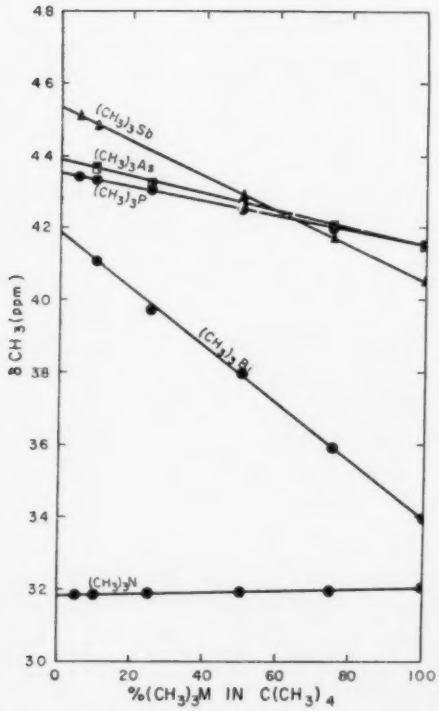

FIG. 2.—Variation of the chemical shift of $(CH_3)_3M$ with concentration in 2,2-dimethylpropane.

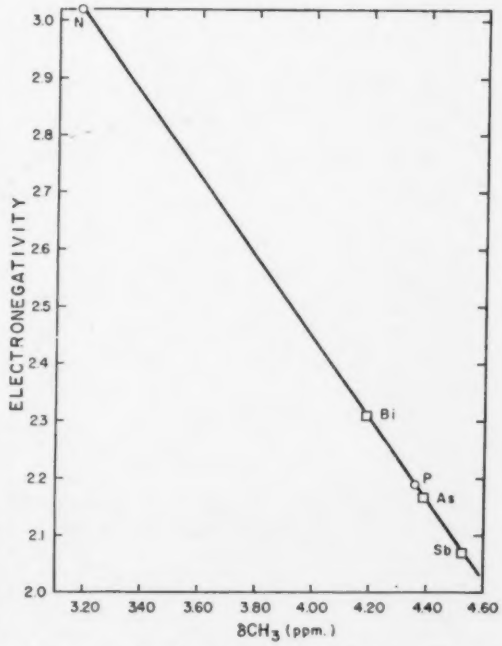

FIG. 3.—Chemical shifts of $(CH_3)_3M$ at infinite dilution in 2,2-dimethylpropane vs. the electronegativity of M.

signals of the Group VB compound and of 2,2-dimethylpropane could not be separated. The reported value for each trimethylphosphine solution corresponds to the center of the doublet produced by spin–spin coupling between ^{31}P and ^{1}H.

Conclusions from chemical shift data. The variation of the proton magnetic resonance frequency of $(CH_3)_3M$, where M is N, P, As, Sb, or Bi, should reflect the electronegativity of M if the bulk magnetic susceptibility, hybridization, and the neighbour-anisotropy effects are constant. Extrapolation of the chemical shift data to infinite dilution ensures a constant bulk magnetic susceptibility effect. The solvent, 2,2-dimethylpropane, is approximately spherically symmetrical and isotropic. The chemical shifts of the methyl halides in 2,2-dimethylpropane vary linearly with concentration.[8] In the analogous series, $(CH_3)_3M$, some variation in the hybridization of M is indicated by the range of C—M—C bond angles. More detailed discussions of the evaluation of electronegativities from chemical shifts appear elsewhere.[1,8]

The electronegativities of the Group VB elements are plotted as a function of the extrapolated proton chemical shift in Fig. 3. The electronegativity values, 3·04 for nitrogen and 2·19 for phosphorus,[4] and a linear relation were assumed.[1] The chemical shifts for $(CH_3)_3As$, $(CH_3)_3Sb$, and $(CH_3)_3Bi$ were used to locate the other points on the line. The *relative* values of electronegativity by this method are 3·04 for nitrogen, 2·19 for phosphorus, 2·17 for arsenic, 2·07 for antimony and 2·31 for bismuth. Only the value for bismuth differs appreciably from the corresponding value on the thermochemical scale. The difference for bismuth may be attributable to the thermochemical value which was calculated from only one datum.

ELECTRONEGATIVITY FROM ELECTROSTATIC CALCULATIONS

Several electrostatic approaches have been employed in the construction of scales of electronegativity. The first method, by GORDY,[9] involves the equation

$$\chi_G = 0{\cdot}31\,\frac{(n+1)}{r} + 0{\cdot}50 \qquad \text{(A)}$$

where n is the number of valence shell electrons and r is the covalent radius. This equation is derived by considering the potential at a distance r from the nucleus which is caused by the nuclear charge effective at that distance. PRITCHARD and SKINNER[10] used a different method of determining effective nuclear charge and suggested the equation

$$\chi_{PS} = a\,\frac{Z_{eff}}{r} + b \qquad \text{(B)}$$

for each period of elements. Electronegativity has been defined[11] as the force of attraction between the nucleus and an electron from a bonded atom and calculated by the equation

$$\chi_A = 0{\cdot}359\,\frac{Z_{eff}}{r^2} + 0{\cdot}744 \qquad \text{(C)}$$

where Z_{eff} is the effective nuclear charge and r is the covalent radius.

[9] W. GORDY, *Phys. Rev.* **69**, 604 (1946).
[10] H. O. PRITCHARD and H. A. SKINNER, *Chem. Rev.* **55**, 745 (1955).
[11] A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 264 (1958).

Electronegativity values obtained from electrostatic calculations are presented in Table 3. The units and the origin of the scales differ slightly. Equations (A), (B) and

TABLE 3.—ELECTRONEGATIVITIES FROM ELECTROSTATICS

	N	P	As	Sb	Bi
G(Eq. A)	3·01	2·19	2·04	1·82	1·83
PS(Eq. B)	3·02	2·20	2·12	1·93	
A(Eq. C)	3·04	2·05	2·18	1·81	

(C), which involve crude models and approximate valuesfor the effective nuclear charges and for covalent radii, are not expected to give precise values of electronegativity. For the calculations involving electrostatic force, an alternation of electronegativity values, χ_A, is observed in the series nitrogen–phosphorus–arsenic–antimony.

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ELECTRONEGATIVITIES FROM WORK FUNCTIONS

GORDY[12] proposed the relation

$$\chi = 0{\cdot}44\phi - 0{\cdot}15$$

where (ϕ) is the work function in electron volts of a metal having an electronegativity χ. Electronegativities obtained from this equation are presented in Table 4. The electronegativity values of arsenic, antimony and bismuth are lower than the values found by most other methods. The crystal structures of the three metals are all rhombohedral; however, these elements probably do not form "pure metallic" bonds and may not obey the equation involving work functions as well as most of the other elements considered by GORDY.

TABLE 4

	As	Sb	Bi
Work function[13] (eV)	5·11	4·08	4·28
Electronegativity	2·09	1·65	1·73

OTHER SCALES OF ELECTRONEGATIVITY

Ionization potentials and electron affinities. MULLIKEN[14,15] proposed that the absolute electronegativity of an atom is equal to the average of its electron affinity and ionization potential for the appropriate valence state. While this method has been used to calculate the electronegativities of several elements,[10] insufficient data involving valence descriptions (amount of *s*-character) and electron affinities has accumulated to permit a comparison of the Group V elements by this method.

Dipole moments. Since the dipole moments of compounds involving Group VB elements would contain contributions, which are not calculable at present, from hybrid bonding orbitals not possessing central symmetry and from lone pairs[16] as

[12] W. GORDY and W. J. O. THOMAS, *J. Chem. Phys.* **24**, 439 (1956).
[13] H. B. MICHAELSON, *J. Appl. Phys.* **21**, 536 (1950).
[14] R. S. MULLIKEN, *J. Chem. Phys.* **2**, 782 (1934).
[15] R. S. MULLIKEN, *J. Chem. Phys.* **46** 497 (1949).
[16] E. A. COULSON, *Proc. Roy. Soc.* A **207** 63 (1951).

well as the contribution from the differences of electronegativities, no attempt was made to evaluate electronegativities from dipole moment data.

Force constants. GORDY[17] suggested the empirical equation, $k = aN(\chi_A\chi_B/d^2)^{0.75}$, where k is the bond-stretching force constant, d the bond length, N the bond order, a and b are constants, and χ_A and χ_B are the electronegativities of bonded atoms. Electronegativity values from this equation are 2·98 for nitrogen, 2·1 for phosphorus, 2·0 for arsenic, 1·8 for antimony and 1·83 for bismuth.

TABLE 5.—SUMMARY OF ELECTRONEGATIVITY SCALES

	N	P	As	Sb	Bi
Thermal data					
Most recent[4]	3·04	2·19	2·18	2·05	2·02
PAULING[7]	3·0	2·1	2·0	1·9	1·9
HAISSINSKY[5] M^{III}	3·0	2·1	2·0	1·8	1·8
M^{V}			2·2	2·1	>2·3
Nuclear magnetic resonance	(3·04)	(2·19)	2·17	2·07	2·31
Electrostatics					
$0{\cdot}31(n+1)/r + 0{\cdot}50$[9]	3·01	2·19	2·04	1·82	1·83
$aZ_{eff}/r + b$[10]	3·02	2·20	2·12	1·93	
$0{\cdot}359Z_{eff}/r^3 + 0{\cdot}744$[11]	3·04	2·05	2·18	1·81	
Work functions[12]			2·09	1·65	1·73
Force constants[17]	2·98	2·1	2·0	1·8	1·83
"Stability ratios"[20]	2·93	2·16	2·53	2·19	
Probable value for M^{III}	3·04	2·19	2·18	2·06	2·16

WALSH[18] defined electronegativity as the stretching force constant of the bond A—H. Due to lack of force constant data and to difficulty in estimating the effect of repulsion between bond and lone pair repulsion, no electronegativity values obtained by this method are presented here.

"*Stability ratio.*" SANDERSON[19,20] proposed that the electronegativity of an atom is determined by its "stability ratio" which he defined as "the ratio of the electron density of an atom or ion to the electron density of an isoelectronic inert atom, real or hypothetical, and determined by interpolation between real values." SANDERSON's relation gives the electronegativity values 2·93 for nitrogen, 2·16 for phosphorus, 2·53 for arsenic and 2·19 for antimony. Thus, "stability ratios" apparently suggest a very large alternation in electronegativity values.

Electronegativity values obtained by the various methods discussed in this paper are compiled in Table 5. The close agreement of the values obtained by widely different procedures is remarkable.

The selection of "best" electronegativity values is somewhat arbitrary. As discussed in a recent review,[10] electronegativity is not an invariant property, and for each element there exists a range of electronegativity values depending on actual valence states. Electronegativities calculated from electrostatics, work functions, and "stability ratios" are invariant for each element. Electronegativity values obtained by thermochemical and nuclear magnetic resonance techniques are different for different

[17] W. GORDY, *J. Chem. Phys.* **14**, 305 (1946).
[18] A. D. WALSH, *Proc. Roy. Soc.* A **207**, 13 (1951).
[19] R. T. SANDERSON, *J. Chem. Educ.* **29**, 539 (1952).
[20] R. T. SANDERSON, *J. Chem. Phys.* **23**, 2467 (1955).

oxidation states but do not reflect a particular type of hybridization (amount of *s*-character). HAISSINSKY calculated[5] by thermochemical methods electronegativities of Group VB elements in pentavalent states, and the recent thermochemical electronegativities at the top of Table 5 are for trivalent states. The electronegativity values from nuclear magnetic resonance studies are for trivalent states. For the most probable electronegativity of each of the Group VB elements in the trivalent state, one may take the average of the values obtained by nuclear magnetic resonance and by the recent thermochemical calculations. Thus, the most probable values for trivalent states are 3·04 for nitrogen, 2·19 for phosphorus, 2·18 for arsenic, 2·06 for antimony and 2·16 for bismuth. For the most probable values of electronegativities of these elements in pentavalent states, one may take HAISSINSKY's values, 2·2 for arsenic, 2·1 for antimony and >2·3 for bismuth.

Only the electronegativity scales based on electrostatic force or on "stability ratios" predict that the electronegativity of trivalent arsenic is greater than that of phosphorus, while seven scales predict the opposite order. Thus, the alternation of electronegativity with period number seems to disappear between Groups IVB and VB.[4] However, the electronegativity of arsenic is practically equal to that of phosphorus. Most of the scales indicate that bismuth is more electronegative than antimony, and the relative values can be explained[4] in terms of the lanthanide contraction. The especially high electronegativity of pentavalent bismuth may be related to the "inert pair."

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CHEMICAL AND PHYSICAL PROPERTIES AND ELECTRONEGATIVITIES

In view of the relative electronegativities, N > P = As > Sb < Bi, the properties of these elements should not always vary monotonically with period number but should exhibit for many cases magnitudes with the order N—P—As—Bi—Sb and for a few other cases magnitudes with the order N—As—P—Bi—Sb. Of course, for chemical and physical behaviour strongly dependent upon other factors, for example bond length or π-bonding, different orders will be observed. This section briefly discusses various properties which should reflect relative electronegativities.

A. *Nuclear quadrupole resonance.* Nuclear quadrupole resonance spectroscopy, reviewed in reference 21, provides information about electron distribution in molecules. The magnitude of the nuclear quadrupole coupling constant, eqQ, for a given isotope depends upon the electric field gradient, q, at the nucleus. The gradient of the electric field at the nucleus is largely caused by unfilled *p*-orbitals.[22,23] Filled shells and *s*-electrons do not produce field asymmetry, and the contribution from *d*-electrons and neighbouring atoms is usually small. For halogens, eqQ is zero for the ions, large for isolated atoms (which have vacant *p*-orbitals), and intermediate for co-valent halogen compounds. Increasing *s* character by hybridization decreases eqQ by increasing spherical symmetry. Also, eqQ is lowered when an unshared pair of electrons on the halogen is involved in double bond formation. It is not possible at present to evaluate separately the magnitude of the various contributions to eqQ. However, a study[24] of forty chlorine-containing compounds indicates a general

[21] W. J. ORVILLE-THOMAS, *Quart. Rev.* **11**, 162 (1957).
[22] C. H. TOWNS and B. P. DAILEY, *J. Chem. Phys.* **17**, 782 (1949).
[23] C. H. TOWNS and B. P. DAILEY, *J. Chem. Phys.* **20**, 35 (1952).
[24] R. LIVINGSTON, *J. Phys. Chem.* **57**, 496 (1953).

dependence of eqQ on electronegativity. As the electronegativity of the atom bonded to the halogen decreases, the magnitude of eqQ decreases.

Figures 4 and 5 show values of eqQ for ^{35}Cl and ^{79}Br in Group VB trichlorides[24] and tribromides,[25] respectively, plotted as a function of the difference in electronegativity[4] of the halogen and the metal. The crystal structures are identical within each series, with the possible exception of the structure of arsenic trichloride. Since comparisons valid for electronegativity studies depend upon identical crystal structures, data are sparse. While other halides of the Group VB elements have been studied, variations in crystal structure preclude those halides from being included here.

In Figs. 4 and 5, the variation of eqQ is linear and monotonic with electronegativity difference and provides additional verification for the electronegativity values employed.

B. *Ionization potentials.* The third, fourth, and fifth ionization potentials[26] of the Group VB elements are plotted as a function of period number in Fig. 6. The zigzag character of the lines and the relatively high ionization potentials of bismuth are evident. A graph of first and second ionization potentials exhibits a similar zigzag character, but the ionization potentials of bismuth are lower than the corresponding values for antimony.

C. *Enthalpy of formation of halides and oxides.* In Figs. 7 and 8, the enthalpies of formation of M_2O_3, M_2O_5, MF_3, and MCl_3 are plotted as a function of period number. With the exceptions of enthalpy values for P_4O_6,[27] PF_3,[28,29] and NCl_3,[30] the data are taken from NBS Circular 500.[31] The data are for the solid states of the oxides, except for dinitrogen trioxide, and for the gaseous states of the halides, except for antimony trifluoride and nitrogen trichloride. Corrections for the heats of fusion and vaporization of these three compounds would not affect the order in Figs. 7 and 8. The observed alternation, commented on by LATIMER and HILDEBRAND[32,33], is readily explainable in terms of electronegativities. The lanthanide contraction is responsible for the compactness of bismuth relative to antimony, and the consequent larger electronegativity of bismuth and lower ionic character of bismuth–halide and bismuth–oxide bonds are reflected by the lower enthalpy of formation of the bismuth compounds. A comparable explanation for the low enthalpy of formation of the arsenic halides and oxides relative to those of phosphorus and antimony can be made in terms of an effect of the transition metal contraction.

D. *Electrical and thermal conductivity.* The electrical conductivities, expressed in Ω^{-1} cm^{-1}, of the Group VB elements are $\sim$0 for phosphorus, $2{\cdot}86 \times 10^4$ for arsenic $2{\cdot}38 \times 10^4$ for antimony, and $0{\cdot}86 \times 10^4$ for bismuth.[34] The opposite trend of conductance with period number for the metal trihalides is frequently quoted as evidence for increasing metallic character in Group VB. The thermal conductivity of

[25] H. ROBINSON, H. G. DEHMELT and W. GORDY, *J. Chem. Phys.* **22**, 511 (1954).
[26] C. E. MOORE, *Atomic Energy Levels*, Vol. 3, p. 34. (Circular 467 of the National Bureau of Standards) U.S. Government Printing Office, Washington, D.C. (1958).
[27] W. E. KOERNER and F. DANIELS, *J. Chem. Phys.* **20**, 113 (1952).
[28] M. BETHELOT, *Ann. Chim. Phys.* **6**, 358 '5).
[29] E. NEALE and L. T. D. WILLIAMS, *J. Chem. Soc.* **53**, 1606 (1957).
[30] L. H. LONG, *Quart. Rev.* **7**, 134 (1953).
[31] F. D. ROSSINI *et al.*, *Selected Values of Chemical Thern.. Dynamic Properties* (Circular 500 of the National Bureau of Standards), U.S. Government Printing Office, Washington, D.C. (1952).
[32] W. M. LATIMER and J. H. HILDEBRAND, *Reference Book of Inorganic Chemistry*, p. 167. Macmillan, New York (1929).
[33] J. H. HILDEBRAND, *J. Chem. Educ.* **18**, 291 (1941).
[34] C. J. SMITHELL, *Metals Reference Book* (2nd Ed.) Interscience, New York (1955).

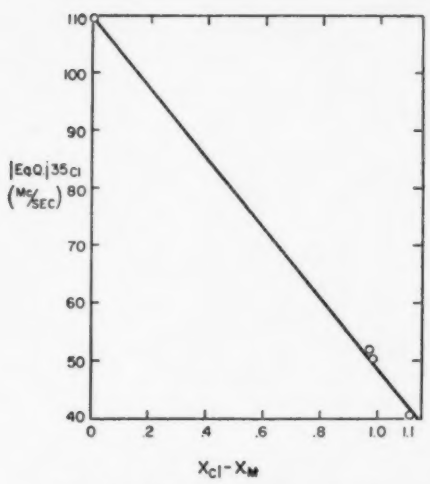

FIG. 4.—Nuclear quadrupole coupling constants of chlorine as a function of the difference of the electronegativities of chlorine and M.

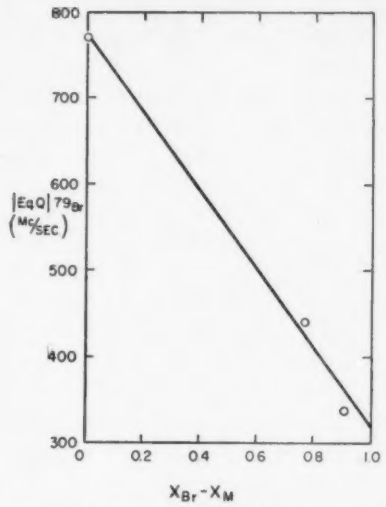

FIG. 5.—Nuclear quadrupole coupling constants of bromine as a function of the difference of the electronegativities of bromine and M.

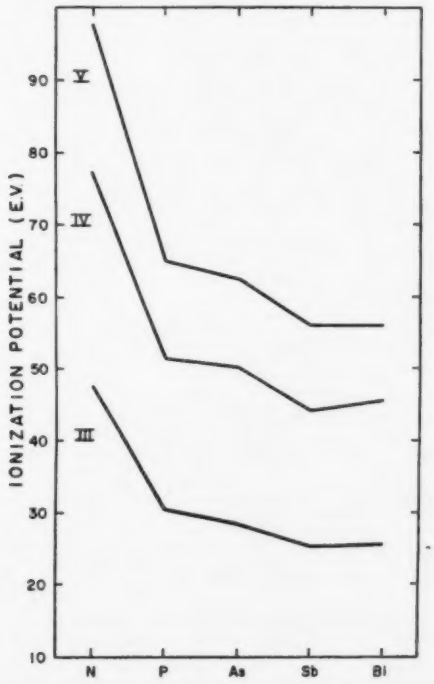

FIG. 6.—Third, fourth, and fifth ionization potentials.

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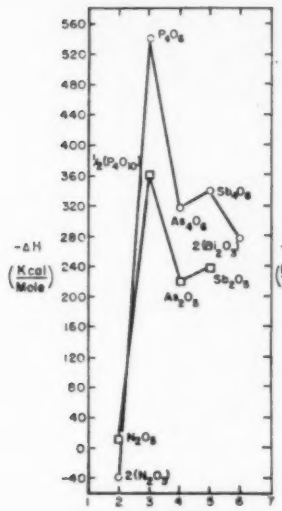

FIG. 7.—$\Delta H^0_{formation}$ of oxides.

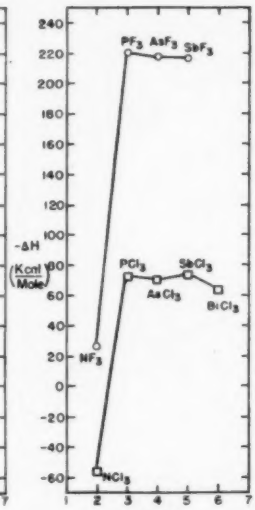

FIG. 8.—$\Delta H^0_{formation}$ of halides.

TABLE 6.—OXIDATION POTENTIALS

Acid solutions	E°
$\frac{1}{2}N_2 + 2H_2O = HNO_2 + 3H^+ + 3e^-$	−1·45
$P + 3H_2O = H_3PO_3 + 3H^+ + 3e^-$	+0·50
$As + 2H_2O = HAsO_2(aq) + 3H^+ + 3e^-$	−0·247
$Sb + H_2O = SbO^+ + 2H^+ + 3e^-$	−0·212
$Bi + H_2O = BiO^+ + 2H^+ + 3e^-$	−0·32
$HNO_2 + H_2O = NO_3^- + 3H^+ + 2e^-$	−0·94
$H_3PO_3 + H_2O = H_3PO_4 + 2H^+ + 2e^-$	+0·276
$HAsO_2 + 2H_2O = H_3AsO_4 + 2H^+ + 2e^-$	−0·56
$2SbO^+ + 3H_2O = Sb_2O_5 + 6H^+ + 4e^-$	−0·581
$2BiO^+ + 3H_2O = Bi_2O_5 + 6H^+ + 4e^-$	ca. −1·6
Basic solutions	
$P + 5OH^- = HPO_3^{-2} + 2H_2O + 3e$	+1·73
$As + 4OH^- = AsO_2^- + 2H_2O + 3e^-$	+0·68
$Sb + 4OH^- = SbO_2^- + 2H_2O + 3e^-$	+0·66
$2Bi + 6OH^- = Bi_2O_3 + 3H_2O + 6e^-$	+0·44
$NO_2^- + 2OH^- = NO_3^- + H_2O + 2e^-$	−0·01
$HPO_3^{-2} + 3OH^- = PO_4^{-3} + 2H_2O + 2e^-$	+1·12
$AsO_2^- + 4OH^- = AsO_4^{-3} + 2H_2O + 2e^-$	+0·67
$SbO_2^- + 5OH^- = H_3SbO_4^{-4} + H_2O + 2e^-$	ca. +0·40

bismuth is also anomalously low: 0·042 (cgs units and 20°C) for antimony and 0·019 for bismuth.[34]

E. *Oxidation potentials.* In Table 6 are listed the standard oxidation potentials[35] for the couples M^0, M^{III} and M^{III}, M^V. Pentavalent bismuth compounds and

[35] W. M. LATIMER, *The Oxidation States of the Elements and Their Potentials in Solutions* (2nd Ed.). Prentice-Hall, New York (1952).

nitric acid are strong oxidizing agents, pentavalent arsenic and antimony compounds are moderately strong oxidizing agents, and phosphoric acid is a very weak oxidizing agent. Trivalent nitrogen and arsenic are usually weaker reducing agents than trivalent phosphorus. Bismuth metal is a poor reducing agent and often occurs uncombined in nature.

F. *A metathetical reaction.* The reaction[36]

$$PCl_3 + AsF_3 \rightarrow PF_3 + AsCl_3$$

has been cited[37] as evidence that the electronegativity of arsenic is greater than that of phosphorus. However, it is clear that the driving force of reaction, as it was carried out in references 36 and 38, is the volatility of phosphorus trifluoride. The boiling points of the trihalides are +74·2°C for PCl_3, +63·°C for AsF_3, −101·5°C for PF_3 and +130·°C for $AsCl_3$. The difference in bond energies, $[E(P—F) + E(As—Cl)] - [E(P—Cl) + E(As—F)] = -2$ kcal/mole;[39] is also noted.

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TABLE 7.—PENTAVALENT HALIDES
[Stable (S), Unstable at 25°C (U), and Unknown (X)]

	F	Cl	Br	I
N	X	X	X	X
P	S	S	S	X
As	S	U	X	X
Sb	S	S	X	X
Bi	S	X	X	X

G. *Oxidation of trialkyl compounds of the group VB elements.* In the preparation of the $(CH_3)_3M$ series in this research, it was observed that trimethylamine and trimethylbismuthine are relatively stable in air at room temperature. Trimethylphosphine and trimethylarsine rapidly decomposed to form trialkyl oxides, while trimethylstibine was oxidised so rapidly that it spontaneously burst into flames. The bismuth compound can be burned but does not produce the alkyl oxide. Also, when trimethylbismuthine and a very limited supply of air were heated, an explosion occurred, and bismuth metal was observed.

H. *Preparation and stability of pentahalides.* A summary of known pentahalides of Group VB elements is presented in Table 7. One may argue that the more electropositive Group VB elements are capable of sharing five valence electrons with chlorine while the less electropositive elements share only three. Therefore, the existence or non-existence of the pentachloride of a Group VB element could be related to the electronegativity of the element; and it would be concluded that nitrogen, arsenic, and bismuth are more electron-attracting in pentavalent states than phosphorus and antimony. In view of arsenic and bromine being in the same period,

[36] M. H. MOISSON, *C.R. Acad. Sci., Paris* **100**, 272 (1885).
[37] R. T. SANDERSON, *J. Amer. Chem. Soc.* **74**, 4792 (1952).
[38] C. J. HOFFMAN, *Inorganic Syntheses*, Vol. 4. p. 149. (Edited by J. C. BAILAR JR.,) McGraw-Hill, New York (1953).
[39] T. L. COTTRELL, *The Strengths of Chemical Bonds* (2nd Ed.) Butterworths Scientific Publications, London (1958).

the instability of arsenic pentachloride may be related to the apparently great instability of perbromates.

CONCLUSIONS

It is very difficult to obtain relative electronegativities, even qualitatively, from chemical behaviour, especially acid-base behaviour, since solubility, solvation, bond length, resonance stabilization, mechanisms, entropy, electronegativity and many other factors influence chemical reactions. In this research, analogous series of compounds containing the Group VB elements were considered, and chemical and physical properties dependent, to some extent, upon electronegativity were observed. The variations of these properties are generally consistent with the electronegativity order $N > P = As > Sb < Bi$ for trivalent states. The most probable electronegativity values for trivalent states are 3·04 for nitrogen, 2·19 for phosphorus, 2·18 for arsenic, 2·06 for antimony and 2·16 for bismuth.

Acknowledgement—We wish to express our appreciation to the Research Corporation for funds used in the purchase of chemicals and equipment.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 55 to 61. Pergamon Press Ltd.

CRYSTAL SPECTRA OF METAL CHELATES—I

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(*Received* 12 *July* 1960; *in revised form* 10 *August* 1960)

Abstract—From the measurement of absorption spectra of crystals of biguanide complexes of copper chloride, -bromide and -fluoride, it has been concluded that the five fold degenerate *d*-orbitals of copper ion are split into four levels by the electrostatic field of the four ligand donor atoms in the plane of the molecule. The electronic transitions between these levels give rise to three absorption bands two of which are both $x(y)$ and z polarized, while the other is only $x(y)$ polarized. The vibronic perturbation which makes these forbidden g-g transitions allowed has been assigned. Similar effect has been noticed with nickel complex, but the analysis was not complete as the whole of the spectrum could not be recorded.

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THE nature of the long wavelength absorption bands in the octahedral complexes of transition metals is now understood fairly well and their assignments to the transitions within the d^n configuration of metal ion have been made from exact theoretical consideration in many cases. The analysis is less complete for square planar and tetragonal complexes as the exact theoretical calculation of the position of the energy levels is rather difficult. Some calculations on these systems have been made by BELFORD *et al.*[1] and by MAKI.[2] Without going into the mathematical details, the nature of the crystal field splitting of the *d*-orbitals may be understood in the following way for copper complexes (i.e., a d^9 system).

Let us take the plane of the molecule as the xy-plane of the cartesian system of co-ordinate with the origin at the copper nucleus. Due to four ligand donor atoms in the xy-plane,—each bond between copper and a donor atom making 45° angles with both x and y-axes—degeneracy of the 3*d*-orbitals will be completely removed. The ligand field theory says that the d_{xy} orbital is much less stable than the other *d*-orbitals since it points directly at the ligands and is made less stable by the electrostatic repulsion of the lone pair electrons on the ligand donor atoms. Electrostatic effect alone will also make the d_{xz}- and d_{yz}-orbitals more stable than $d_{x^2-y^2}$. Under these circumstances d_{z^2}-orbital will be as stable as or more stable than d_{xz} and d_{yz}-orbitals which will remain degenerate. In solution, however, some amount of solvent-solute interaction is always present and the incipient solvation at the axial positions makes the d_{z^2}-orbital less stable than $d_{xz}(d_{yz})$. (Similar situation exists in solvated crystals). But whether the d_{z^2} level is raised above $d_{x^2-y^2}$ or not is a debatable question. BELFORD *et al.*[1] and BASU and BASU[3] assumed that in the case of square planar copper complexes in solution the d_{z^2}-level is raised above $d_{x^2-y^2}$. The energy level diagram for square planar copper complex is shown in Fig. 1. The electronic transitions between these levels give rise to three absorption bands designated as ω_1, due to the transition from $d_{yz}(d_{xz})$ to d_{xy}; ω_2, to the transition from $d_{x^2-y^2}$ to d_{xy} and ω_3, to the transition from d_{z^2} to d_{xy}. The band ω_1 has the shortest wavelength and

[1] R. L. BELFORD, M. CALVIN and G. BELFORD, *J. Chem. Phys.* **26**, 1171 (1957).
[2] G. MAKI, *J. Chem. Phys.* **28**, 651 (1958); **29**, 162, 1129 (1958).
[3] G. L. BASU and S. BASU *Z. Phys. Chem.* In press.

ω_3 the longest with ω_2 in between. Now let us analyse how these bands will behave if the field strength of the two axial ligands, placed along the z-axis, is changed. For invariant in-plane ligand positions increasing base strength of the axial ligands will not appreciably affect d_{xy} and $d_{x^2-y^2}$, but will raise the d_{z^2} and $d_{xz}(d_{yz})$ levels. The transition ω_2 will thus be unaffected, but ω_1 and ω_3 will decrease in energy. Thus on passing from a non-polar to a polar medium ω_1 and ω_3 will show red shift, while ω_2 will be unaffected. Increase in in-plane base strength will similarly affect the d_{xy} and $d_{x^2-y^2}$ levels most, therefore there will be blue shift in the ω_1 and ω_2 bands.

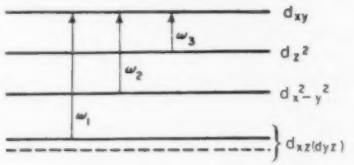


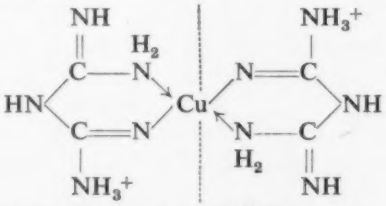
FIG. 1.

All these expectations have been well verified by BELFORD *et al.*[1] and by BASU and BASU[3] from the measurement of absorption spectra of a number of square planar copper complexes in various polar and non-polar organic solvents, which is at the basis of their assignment of the energy levels shown in Fig. 1.

It must be mentioned that the spectrum of square planar copper complexes in solution consists of one broad band in most cases and the component peaks are located by a Gaussian analysis. This resolution can not be claimed to be unique. The situation will be happier if the component peaks could be located experimentally or if the band shows sufficient structure to make the resolution into Gaussian components unique. Such a situation may be obtained in the absorption spectrum of the complexes in their crystalline state. Further the polarization selectivity of the various band systems of the crystal spectrum may supply useful information to make the assignment of the various *d-d* transitions more or less complete. With this object in view absorption spectra of copper and nickel biguanides were measured in their crystalline state the results of which are reported in the present paper.

BIGUANIDE COMPLEXES OF COPPER AND NICKEL

The biguanide complexes of transition elements have been studied by RÂY and co-workers.[4,5] Copper chloride, bromide and fluoride form rose-red complexes which crystallise with two molecules of water. The complexes have been formulated as $[Cu(C_2N_5H_7)_2 \cdot 2H_2O]X_2$. (The fluoride complex separates with four molecules of water, two with cation and two with anion). The structure of the planar $[Cu(C_2N_5H_7)_2]^{2+}$ ion is as follows:



[4] P. RÂY and P. N. BAGCHI, *J. Indian Chem. Soc.* **16**, 617 (1939).
[5] P. RÂY and B. C. PURAKAYASTHA *J. Indian Chem. Soc.* **18**, 217 (1941).

with two water molecules presumably on the dotted line which is perpendicular to the rest of the complex cation.

The absorption spectra of the dihydrate in the crystalline state are shown in Figs. 2–4 with light polarized parallel and perpendicular to the long axis of the

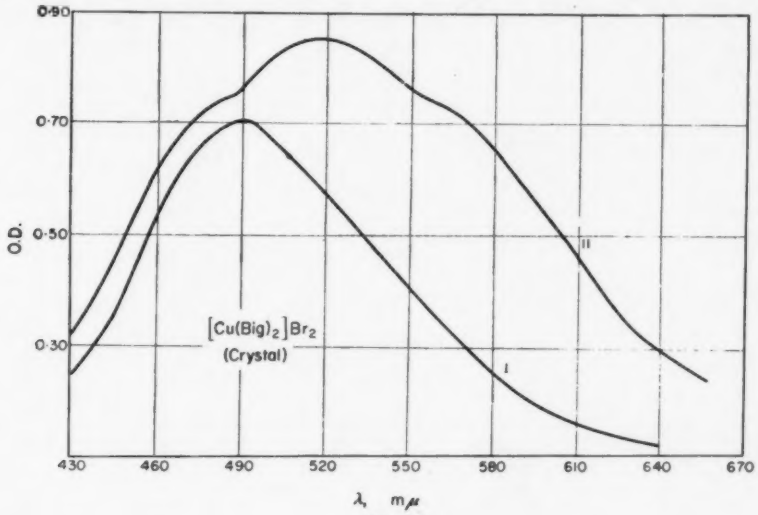


FIG. 2.

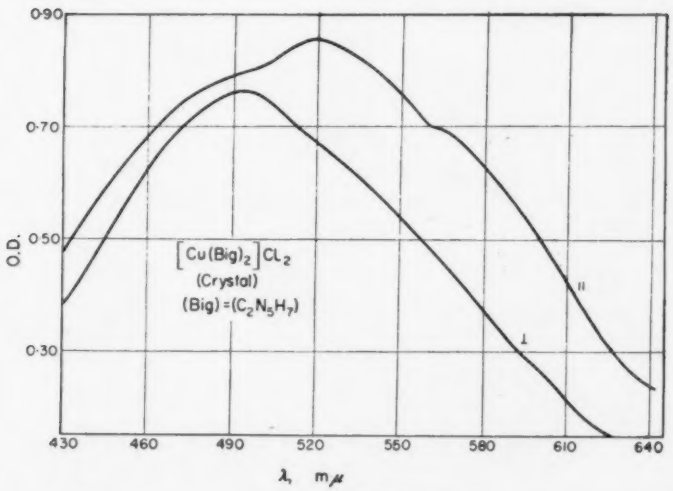


FIG. 3.

crystal. It is evident that the bands have well defined structures, unlike solution spectrum (Fig. 5). The resolution of the band into component Gaussian bands was simple and more definite. The position of the peaks are summarized in the Table 1. It may be observed that as expected from the theoretical considerations the absorption spectrum consists of three bands in all cases. The peaks of these bands appear at about the same positions with chloride, bromide and fluoride, indicating thereby

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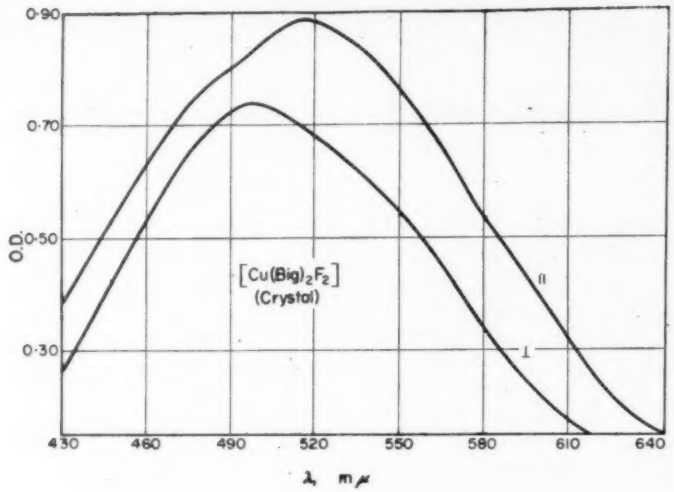

FIG. 4.

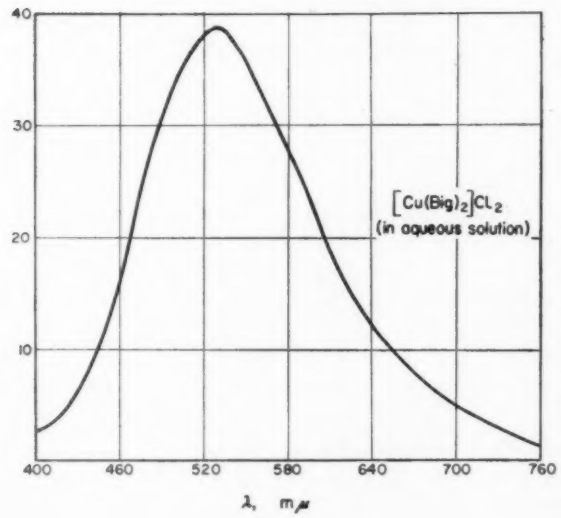

FIG. 5.

TABLE 1.—PEAKS OF THE GAUSSIAN BANDS IN COPPER BIGUANIDES

Compound	λ_1(mμ)	λ_2(mμ)	λ_3(mμ)	State of polarization of incident light
Copper bis-biguanide dichloride	495	555	580	∥
	495	555	—	⊥
Copper bis-biguanide dibromide	490	545	575	∥
	490	545	—	⊥
Copper bis-biguanide difluoride	495	555	570	∥
	495	555	—	⊥

that the halide ion exists outside the co-ordinating sphere of the copper ion and exerts no perturbing action on the *d*-orbitals of copper.

As all these transitions involve *d*-orbitals they are evidently forbidden *g-g* transitions made allowed by vibronic perturbation. If the type of vibrational coupling responsible for this perturbation could be assigned, the polarisation selectivity of the transitions could be interpreted. The transformation properties of the orbitals of the central metal ion in the complex is given in the Table 2. The symmetry of the ground and excited configurations involving *d*-orbitals are also given in the same table.

TABLE 2.—SYMMETRY CLASSIFICATION[6]

Atomic orbital	s	P_xP_y	P_z	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz}(d_{yz})$
Symmetry type	A_{1g}	E_u	A_{2u}	A_{1g}	B_{1g}	B_{2g}	E_g

Transition	Configuration symmetry
$d_{xz}(d_{yz}) \rightarrow d_{xy}$	$B_{2g} \rightarrow E_g$
$d_{z^2} \rightarrow d_{xy}$	$B_{2g} \rightarrow A_{1g}$
$d_{x^2-y^2} \rightarrow d_{xy}$	$B_{2g} \rightarrow B_{1g}$

From quantum mechanical considerations it can be shown that an electronic transition will be allowed if the ground or the excited state configuration has the same symmetry as one of the cartesian co-ordinates. The symmetry of z-axis is A_{2u} and that of x (and y) axis is E_u. It is evident from the Table 2 that none of the transitions involving *d*-orbitals has the proper symmetry to make them allowed. Therefore the only way they can be made allowed is by vibronic perturbation. In the Table 3 are given

TABLE 3.—SYMMETRY OF VIBRATION[6]

Types of vibration	Stretching			Bending			
				in-plane		out-of-plane	
Symmetry type	A_{1g}	B_{1g}	E_u	B_{2g}	E_u	A_{2u}	B_{2u}

the various modes of vibrations and their symmetry for a square planar complex. One stretching mode which can couple with the excited configurations to give proper translational symmetry is E_u. Similar is the case with in-plane bending vibration. The out-of-plane bending vibration of symmetry B_{2u} can couple with two of the excited configurational wave functions to give translational symmetry. The results are given below. It is evident from the Table 4 that $d_{xz}(d_{yz})$ to d_{xy} and $d_{x^2-y^2}$ to d_{xy} transitions are both $x(y)$ and z polarized, while the d_{z^2} to d_{xy} transition is only $x(y)$ polarized. It is to be noticed from the Figs. 2–4 that the longest wavelength absorption band near 580 mμ of copper biguanides is uniquely polarized along the long axis of the crystal, while the two others at about 495 mμ and 555 mμ are both short and long axis polarized. We may therefore associate the longest wavelength band with $d_{z^2} \rightarrow d_{xy}$ transition, an assignment that has also been made qualitatively from the energy considerations. (As the complete crystal structure is not known, this remains as a plausible suggestion for the present.) Similar assignments have been made by CHATT *et al.*[6] from the consideration of polarization selectivity of the absorption bands of some platinous complexes.

[6] J. CHATT, G. A. GAMLEN and L. E. ORGEL *J. Chem. Soc.* 486 (1958)

TABLE 4.—SYMMETRY OF THE EXCITED STATES AND OF THE VIBRATIONS MAKING TRANSITION TO THEM ALLOWED

Vibration	Transition	Symmetry of the excited state	Symmetry of vibration	Polarization
Stretching and in-plane bending	$d_{xz}(d_{yz}) \rightarrow d_{xy}$	E_g	E_u	z
	$d_{z^2} \rightarrow d_{xy}$	A_{1g}	E_u	x,y
	$d_{x^2-y^2} \rightarrow d_{xy}$	B_{1g}	E_u	x,y
Out-of-plane bending	$d_{xz}(d_{yz}) \rightarrow d_{xy}$	E_g	B_{2u}	x,y
	$d_{x^2-y^2} \rightarrow d_{xy}$	B_{1g}	B_{2u}	z

Nickel forms diamagnetic complexes with biguanide similar to copper. As these complexes are square planar we may assume that the splitting of the *d*-orbitals will be approximately similar to that of copper, although the normal singlet band systems may be associated with triplet ones at longer wavelength. In the Fig. 6 is shown the

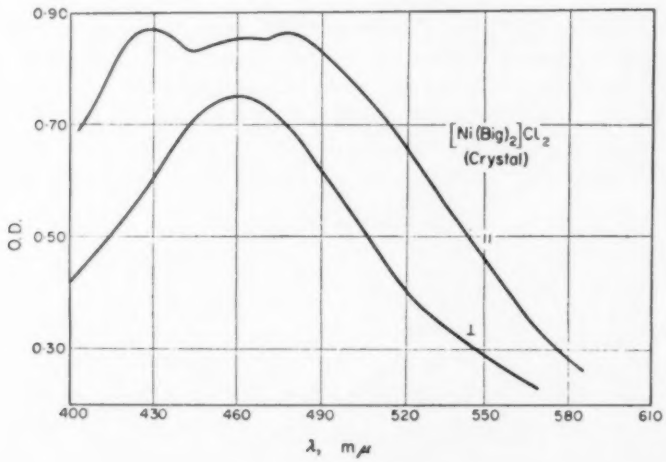

FIG. 6.

absorption spectrum of a crystal of biguanide complex of nickel chloride. With light polarized along the long axis of the crystal the nature of the absorption spectrum suggests that it is made up of at least three component bands. Its resolution by Gaussian method is not completely possible as a part of the band extends well below 400 mμ, i.e., into the region inaccessible to our instrument. The triplet band in the long wavelength side was not observed.

As the ground and the excited configurations have symmetries different from those of copper complexes, the polarization selectivity of the bands will be different in two cases. It can be shown that in this case two of the long wave transitions are both $x(y)$ and z polarized, while the shortest wave band is only $x(y)$ polarized. From the Fig. 6 it is evident that with light polarized along the short axis of the crystal the short wave band is missing from the absorption spectrum. As a complete Gaussian analysis of the absorption band could not be made, the detailed assignment is postponed for the present.

EXPERIMENTAL

Preparation of the complexes

An ammoniacal solution of copper sulphate was treated with a solution of biguanidine sulphate containing excess sodium hydroxide, when a bright silky precipitate of the complex base $[Cu(C_2N_5H_7)_2](OH)_2$ was obtained. The dried powdered base was heated with 15 per cent ammonium chloride solution on a water bath. The clear solution was filtered hot and on cooling crystals of chloride $Cu(C_2N_5H_7)_2]Cl_2 \cdot 2H_2O$ separated out. The bromide and fluoride complexes were obtained by heating the base with ammonium bromide and fluoride respectively. The nickel complex was obtained by an analogous procedure. Details are given in literature.[4,5] The crystals were obtained by slow evaporation of a dilute aqueous solution of the complex and were dried in air. Crystals having thickness in the range 0·08–0·07 mm (measured by microscopic technique) were used for spectral study. The reagents were all AnalaR quality samples.

Measurement of absorption spectra

The absorption spectra of solutions were measured in a Beckman Spectrophotometer Model DU using 1 cm corex cells. Tungsten light source was used in all cases. The instrument was calibrated with sodium yellow and mercury green lines.

The absorption spectra of crystals were measured using the microscopic technique developed and described by Japanese workers.[7] The light source was a R.C.A. strip filament projection lamp, which was used in conjunction with a Hilger's constant deviation glass prism monochromator. Light of wavelength 400 mμ to 700 mμ could be isolated at an interval of 1–2·5 mμ. The monochromatic beam of light was reflected by a front surface mirror on to the stage of a polarizing microscope from below. The crystal was placed on the stage over a glass slide and the transmitted beam of light was viewed through the eye piece. The objective-eyepiece combination produced a magnification of 60× and the crystals were so selected as to cover the field of vision completely.

After necessary adjustments had been made the eye was replaced by a photomultiplier tube assembly. The phototube was a RCA 1P21 photomultiplier tube and was used in conjunction with a Plymale and Hansen's (NRL Report 3555) Linear d.c. Amplifier and the stabilized voltage source. The power supply using electronic voltage stabilization and control provided a dynode voltage which could be varied from 80 to 100 V per stage. (80 V per stage were used in all measurements). A bridge circuit with high impedance input amplified the current from the phototube, so that an optimum overall performance was obtained with a meter in the output circuit. Dark current was balanced manually and a nine position gain switch with a stage-to-stage ratio of about 5X was used to control the sensitivity. A calibration curve was maintained for the scale ratio.

The polarization selectivity of the absorption band was tested either by rotating a polarizer placed below the stage or by rotating the analyser placed above the objective or by keeping the polarizer fixed and rotating the stage with the crystal through 90°. Same result was obtained in all these operations. For the sake of convenience the analyser was rotated in most cases. All measurements were made at room temperature (about 27°C).

The Gaussian analysis was made on O.D. vs. λ curve using LOWRY and HUDSON'S[8] equation following a method suggested by CHATT *et al.*

[7] R. TSUCHIDA and M. KOBAYASHI *Bull. Japan Chem. Soc.* **13**, 388 (1938).
[8] T. M. LOWRY and H. HUDSON *Phil. Trans.* A **232**, 117 (1933).

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 62 to 68. Pergamon Press Ltd.

SULPHOXIDES AS LIGANDS—III

DIMETHYLSULPHOXIDE COMPLEXES OF Co(II) AND Ni(II) CONTAINING TETRAHEDRAL TETRAHALO ANIONS

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(*Received* 22 *August* 1960)

Abstract—The preparation of the compounds $[Co(DMSO)_6]I_2$, $[Co(DMSO)_6][CoI_4]$, $[Co(DMSO)_4][Co(NCS)_4]$, $[Co(NCS)_2(DMSO)_4]$ $[Ni(DMSO)_6]Br_2$, $[Ni(DMSO)_6][NiBr_4]$, $[Ni(DMSO)_6][NiBr_4]\cdot 2DMSO$, $[Ni(DMSO)_6]I_2$, $Ni(DMSO)_4I_2$, $Ni(DMSO)_4(NCS)_2$ and $Ni(DMSO)_4(ONO_2)_2$ is reported and structural assignments are suggested on the basis of spectral and magnetic data which are also reported. The formulas as written above indicate the proposed structures and the anions $[CoI_4]^{2-}$, $[Co(NCS)]_4^{2-}$ and $[NiBr_4]^{2-}$ are believed to be tetrahedral.

IN a preceding paper[1] in this series a large number of complexes of dimethyl sulphoxide were reported. Among them were a few of cobalt (II) and nickel (II) salts, viz., $[Co(DMSO)_6](ClO_4)_2$ $[Co(DMSO)]_6I_2$ and $[Ni(DMSO)_6](ClO_4)_2$, which were postulated to contain the octahedral $[M(DMSO)_6]^{2+}$ ions indicated in the formulas as written, as well as $CoCl_2\cdot 3DMSO$, $CoBr_2\cdot 3DMSO$ and $NiCl_2\cdot 3DMSO$, of which the first and last were shown to be $[Co(DMSO)_6][CoCl_4]$ and $[Ni(DMSO)_6][NiCl_4]$ respectively, with the $[MCl_4]$ anions being tetrahedral. In this paper we report the preparation of other dimethylsulphoxide complexes of Co(II) and Ni(II) and describe detailed spectral and magnetic studies which permit us to consider structural assignments for them. Some of the new compounds are shown to contain tetrahedral $[CoBr_4]^{2-}$, $[CoI_4]^{2-}$, $[Co(NCS)_4]^{2-}$ and $[NiBr_4]^{2-}$ anions.

RESULTS AND DISCUSSION

Cobalt(II) *compounds*

We shall consider first the cobaltous complexes. We have previously[1] reported the compounds $Co(ClO_4)_2\cdot 6DMSO$ (pink) and $CoCl_2\cdot 3DMSO$ (deep blue) and presented evidence to show that the former contains the cation $[Co(DMSO)_6]^{2+}$ and that the latter has the constitution $[Co(DMSO)_6][CoCl_4]$.

In the CoI_2–DMSO system, we have isolated two compounds. Red $CoI_2\cdot 6DMSO$ should, evidently, be formulated as $[Co(DMSO)_6]I_2$. Its magnetic moment of 5·00 BM, like the moment of 5·02 BM for $[Co(DMSO)_6](ClO_4)_2$ is quite consistent with this formulation.[2,3,4,5] Moreover, the reflectance spectra of the two compounds are quite similar (Fig. 1) and both closely resemble the spectra of Co^{2+} ions in DMSO and in H_2O (Fig. 1) in which it seems safe to assume that only the species $[Co(DMSO)_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$ are present.

[1] F. A. COTTON and R. FRANCIS, *J. Amer. Chem. Soc.* **82**, 2986 (1960).
[2] R. H. HOLM and F. A. COTTON, *J. Chem. Phys.*, **31**, 788 (1959).
[3] R. H. HOLM and F. A. COTTON, *J. Chem. Phys.* **32**, 1168 (1960).
[4] F. A. COTTON and R. H. HOLM, *J. Amer. Chem. Soc.* **82**, 2979 (1960).
[5] F. A. COTTON and R. H. HOLM, *J. Amer. Chem. Soc.* **82**, 2983 (1960).

The green substance, $CoI_2 \cdot 3DMSO$, obtained by long pumping on $CoI_2 \cdot 6DMSO$ at 80°, should be formulated as $[Co(DMSO)_6][CoI_4]$, according to the following evidence. The spectrum is compared in Fig. 2 with the spectra of $[Co(DMSO)_6](ClO_4)_2$ and quinolinium (QH) tetraiodocobaltate(II). It will be seen that, within the limits which may be expected in comparing reflectance spectra, the spectrum of

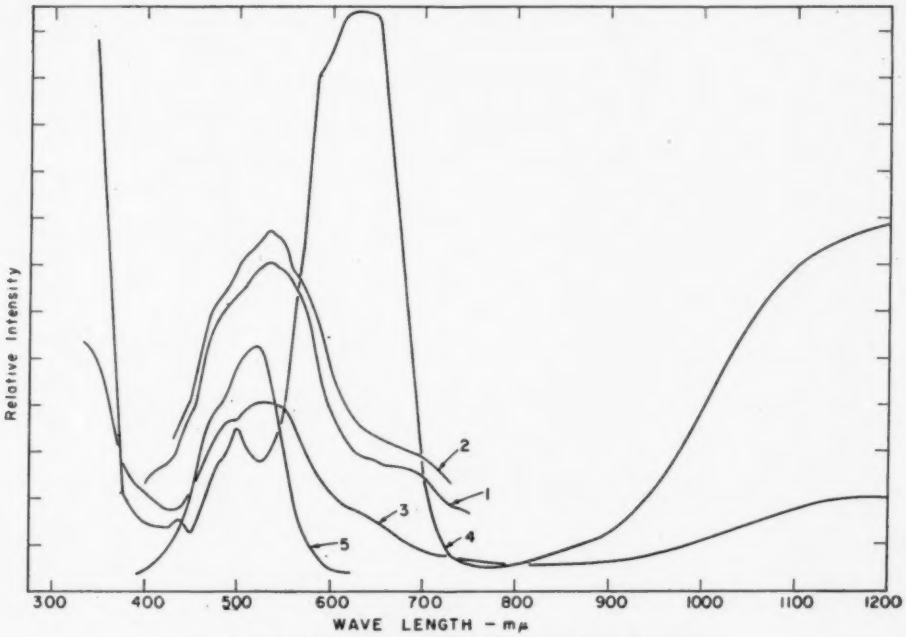

FIG. 1.—Visible spectra of some DMSO complexes of Co(II)
1. Reflectance spectrum of $[Co(DMSO)_6](ClO_4)_2$
2. Reflectance spectrum of $[Co(DMSO)_6]I_2$
3. Reflectance spectrum of $Co(NCS)_2 \cdot 4DMSO$
4. Reflectance spectrum of $[Co(DMSO)_6][Co(NCS)_4]$
5. The spectrum of $[Co(H_2O)_6]^{+2}$ (0·11 molar aqueous solution).

$CoI_2 \cdot 3DMSO$ appears to be a superposition of the spectra of $[Co(DMSO)_6](ClO_4)_2$ and $(QH)_2[CoI_4]$. The $[CoI_4]^{2-}$ ion in the latter compound has been shown to be tetrahedral by magnetic and spectral measurements.[2] Magnetic data also support the proposed formulation. Holm and Cotton report the moment of $[CoI_4]^{2-}$ to be 5·01 ± 0·05 BM,* while the moment of $[Co(DMSO)_6](ClO_4)_2$ has been previously reported[1] by us to be 5·01 ± 0·05 BM. Thus the moment of 5·02 BM, calculated from the susceptibility, for "$CoI_2 \cdot 3DMSO$" is quite consistent with the structure $[Co(DMSO)_6][CoI_4]$.

The compound $CoBr_2 \cdot 3DMSO$ was reported but not structurally characterized in a previous paper[1] on sulphoxide complexes. By arguments similar to those used for $[Co(DMSO)_6][CoCl_4]$ and $[Co(DMSO)_6][CoI_4]$ (*vide supra*) it can be shown that

* If the Weiss constant [4] of −16°K found in $(QH)_2[CoI_4]$ were entirely ignored, the moment would be 4·91 BM. It is impossible to take account of the effects of Weiss constants in the various compounds in any truly rigorous way, but their magnitudes are not such as to make this a serious difficulty from a practical viewpoint.

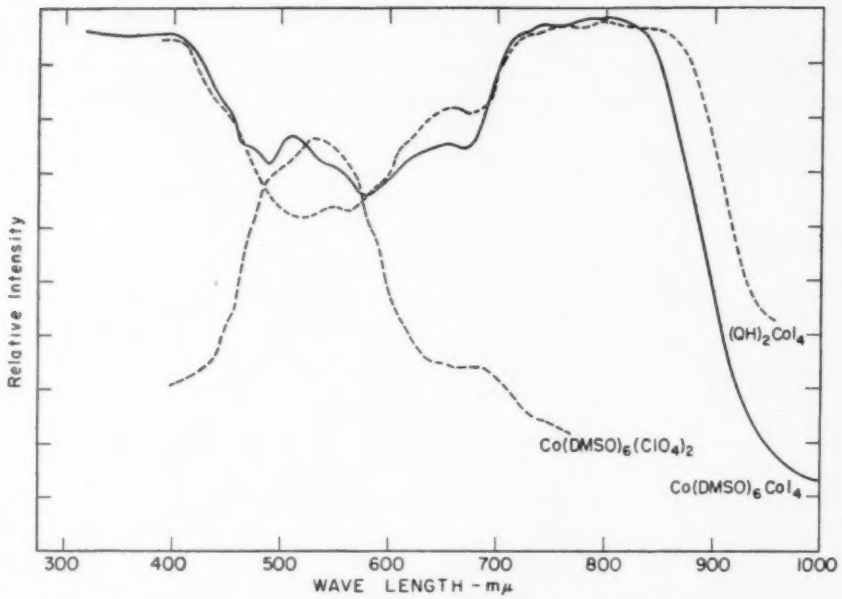

FIG. 2.—The reflectance spectrum of $[Co(DMSO)_6][CoI_4]$ together with reflectance spectra of quinolinium tetraiodocobaltate(II) and $[Co(DMSO)_6](ClO_4)_2$ for comparison.

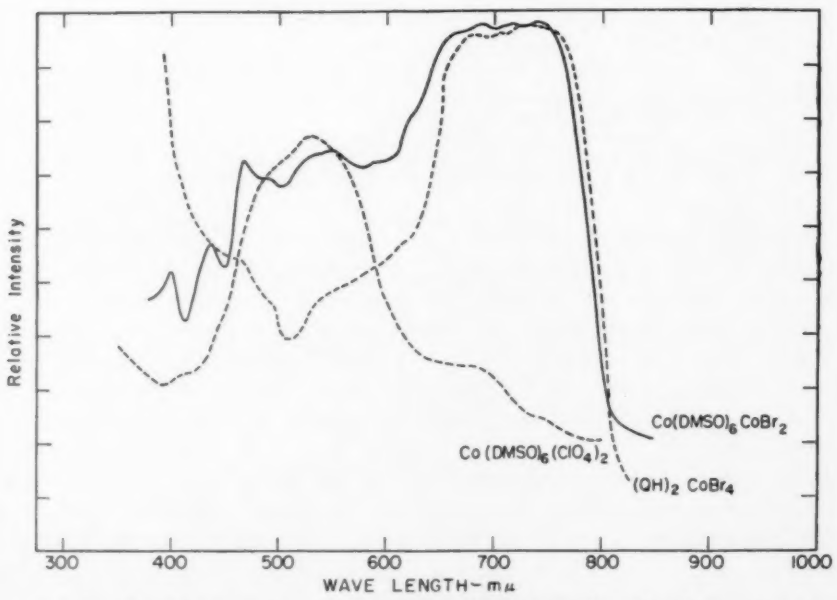

FIG. 3.—The reflectance spectrum of $[Co(DMSO)_6][CoBr_4]$ together with reflectance spectra of quinolinium tetrabromocobaltate(II) and $[Co(DMSO)_6](ClO_4)_2$ for comparison.

this compound should be formulated $[Co(DMSO)_6][CoBr_4]$. In Fig. 3 are the reflectance spectra of the compound together with those of $[Co(DMSO)_6](ClO_4)_2$ and $(QH)_2[CoBr_4]$. As in the other cases, the spectra of the last two can be superposed to give a very good facsimile of the spectrum of $[Co(DMSO)_6][CoBr_4]$. Again, the magnetic moment of the compound provides confirmation for this structure. We should expect the moment to be approximately the root-mean-square of the moments of $[Co(DMSO)_6]^{2+}$ and $[CoBr_4]^{2-}$, which, taking for the former $5{\cdot}02 \pm 0{\cdot}05$ BM[1] and for the latter $4{\cdot}86 \pm 0{\cdot}05$ BM,[2] would be $4{\cdot}94 \pm 0{\cdot}10$. This agrees, within the errors, with the measured value of $4{\cdot}85 \pm 0{\cdot}05$.

The two complexes of cobalt(II) thiocyanate, $Co(NCS)_2{\cdot}3DMSO$ and $Co(NCS)_2{\cdot}4DMSO$, may be assigned quite different structures on the basis of their magnetic moments and spectra. They provide an excellent illustration of the use of such criteria for inferring structures of Co(II) compounds. The compound $Co(NCS)_3{\cdot}3DMSO$ has an intense blue colour and its reflectance spectrum, Fig. 1, shows the intense absorption at ~625 mμ characteristic of the $[Co(NCS)_4]^{2-}$ ion.[6,7] The high frequency tail of this strong band practically obscures the weak absorption at 535 mμ due to the $[Co(DMSO)_6]^{2+}$ ion which is also present in the structure $[Co(DMSO)_6][Co(NCS)_4]$. The magnetic moment provides, in this case, definite corroboration of the proposed structure. The root-mean-square of the values $5{\cdot}02 \pm 0{\cdot}05$ BM for $[Co(DMSO)_6]^{2+}$ and $4{\cdot}46 \pm 0{\cdot}05$ BM for $[Co(NCS)_4]^{2-}$[3] is $4{\cdot}74 \pm 0{\cdot}10$ BM, which is in excellent agreement with the experimental value of $4{\cdot}74 \pm 0{\cdot}05$ BM.

$Co(NCS)_2{\cdot}4DMSO$, on the other hand, contains no tetrahedral species. Its visible absorption spectrum (Fig. 1) closely resembles that of other spin-free octahedral or tetragonal[4] cobalt(II) complexes. Moreover, the high magnetic moment, is good evidence against the presence of any $[Co(NCS)_4]^{2-}$ ion and is typical of moments found in other octahedral and tetragonal cobalt(II) complexes.[4,5]

Nickel(II) compounds

The compounds $[Ni(DMSO)_6](ClO_4)_2$ and $[Ni(DMSO)_6][NiCl_4]$ have been reported previously, and evidence presented for the formulations given above. Several new compounds have subsequently been prepared and characterized.

Nickel bromide combines with DMSO to form three different compounds. The light green compound $NiBr_2{\cdot}6DMSO$ can probably be formulated as $[Ni(DMSO)_6]Br_2$, but it is difficult to obtain pure samples reproducibly and in quantity and it has not been investigated magnetically. The reflectance spectrum of a solid sample which had a good analysis had peaks at 413 (sharp), 750 (very flat on top) and 1300 (broad) mμ. This spectrum is in agreement with the suggested formulation, but does not of course exclude $[Ni(DMSO)_4Br_2]{\cdot}2DMSO$ for example.

On heating $NiBr_2{\cdot}6DMSO$, or material approximating to this composition, in vacuum at 61° it goes very rapidly over to a light blue substance analyzing well as $NiBr_2{\cdot}4DMSO$. This, upon prolonged pumping at 80°, loses a further mole of DMSO giving $NiBr_2{\cdot}3DMSO$ which is dark green. The effective magnetic moments of these compounds at room temperature are 3·78 and 3·67 BM respectively, which would

[6] T. Dreisch and W. Trommer, *Z. Phys. Chem.* B 37, 37 (1937).
[7] F. A. Cotton, D. M. L. Goodgame, M. Goodgame, A. Sacco, *J. Amer. Chem. Soc.* In press.

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suggest the presence of tetrahedrally coordinated nickel(II) in both.[8,9] This is supported by the reflectance spectra. Fig. 4 shows the reflectance spectra of $NiBr_2 \cdot 4DMSO$ and $[(C_2H_5)_4N]_2[NiBr_4]$; from the comparison it would appear that $NiBr_2 \cdot 4DMSO$ most likely contains the $[NiBr_4]^{2-}$ ion. $NiBr_4 \cdot 3DMSO$ has failed to give a sharp, well-resolved reflectance spectrum, but a flat-topped absorption centering at 735–740 mμ is not inconsistent with the presence of the $[NiBr_4]^{2-}$ ion in this

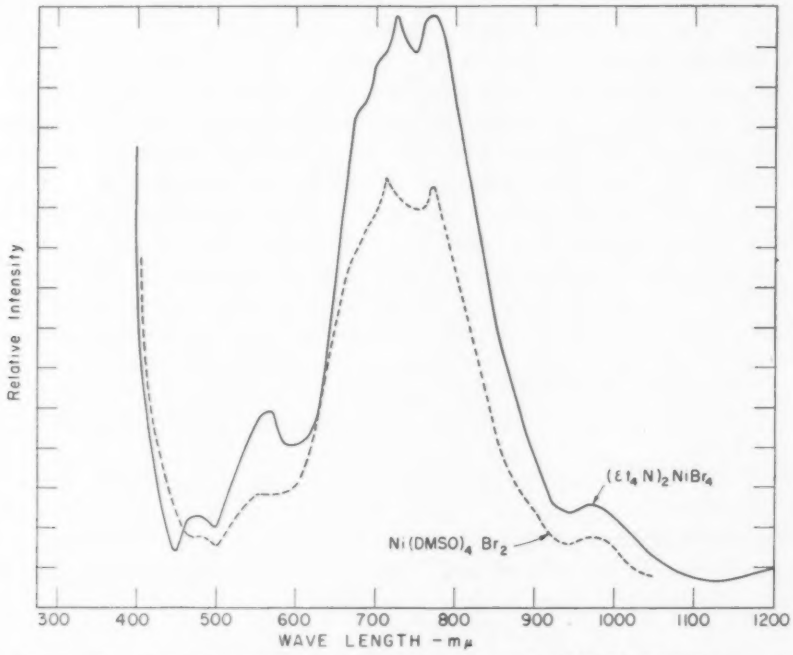

FIG. 4.—The reflectance spectra of $NiBr_2 \cdot 4DMSO$ (———) and $[(C_2H_5)_4N]_2[NiBr_4]$ (-----).

compound. The infrared spectra of the compounds are virtually identical. We believe that these facts may best be explained by postulating the structures $[Ni(DMSO)_6][NiBr_4] \cdot 2DMSO$ and $[Ni(DMSO)_6][NiBr_4]$ for these compounds.

While the compound $NiI_2 \cdot 6DMSO$ is difficult, perhaps impossible, to isolate in an analytically pure state owing to its instability, a reflectance spectrum which is probably authentic has been obtained. It has a peak at 400 mμ, a doublet at ~680 and 750 mμ and a broad peak at ~1200 mμ. The spectrum thus resembles those of $[Ni(H_2O)_6]^{2+}$ and of Ni(II) in liquid DMSO and it is reasonable to suppose that the $[Ni(DMSO)_6]^{2+}$ ion with Ni-O linkages is present. On heating in vacuum $NiI_2 \cdot 6DMSO$ rapidly loses DMSO giving $NiI_2 \cdot 4DMSO$ in which the effective magnetic moment of the nickel at room temperature is 3·16 BM. The reflectance spectrum has a broad peak at ~450 mμ and a very broad one at ~850 mμ. These observations suggest that the structure is $[Ni(DMSO)_4]I_2$ or $[Mi(DMSO)_4I_2]$ and rule out the presence of $[NiI_4]^{2-}$ ion.

The only DMSO complex obtained using $Ni(CNS)_2$ is $Ni(CNS)_2 \cdot 4DMSO$. Here

[8] N. S. GILL and R. S. NYHOLM, *J. Chem. Soc.* 3997 (1959).
[9] F. A. COTTON and D. M. L. GOODGAME *J. Amer. Chem. Soc.* **82**, 5771, 5774 (1960).

again the magnetic moment (3·22 BM at 25°) and the reflectance spectrum which has peaks at 400 mμ, 665 mμ, ~750 mμ(sh) and ~1125 mμ (very broad) indicate the absence of any tetrahedral species and suggest either $[Ni(DMSO)_4(NCS)_2]$ or $[Ni(DMSO)_4](NCS)_2$ as likely structures. Similarly, $Ni(NO_3)_2 \cdot 4DMSO$ would appear on the basis of its magnetic moment (3·15 BM at 25°) and reflectance spectrum (bands at 410 mμ, ~690(sh) mμ, 755 mμ and 1300 mμ (very broad)), which closely resembles the spectra of $[Ni(H_2O)_6]^{2+}$ and Ni(II) in DMSO, to have the structure $[Ni(DMSO)_4(ONO_2)_2]$.

EXPERIMENTAL

Preparation of compounds

$CoI_2 \cdot 3DMSO$. On heating it in vacuum at 80° for 36 hours, $CoI_2 \cdot 6DMSO$ yields the light green substance $CoI_2 \cdot 3DMSO$. (Found: Co, 10·77; I, 46·35; C, 13·15; H, 3·31. Calc. for $C_{12}H_{36}S_6O_6CoI_2$: Co, 10·77; I, 46·39; C, 13·17; H, 3·32%).

$Co(NCS)_2 \cdot 4DMSO$. It is found that 2·29 g (0·01 mole) of $Co(NCS)_2 \cdot 3H_2O$ (from metathesis of $CoSO_4 \cdot 6H_2O$ and $Ba(NCS)_2 \cdot 2H_2O$) is readily soluble in 2·8 g (0·1 mole) of DMSO to give a deep blue solution. Upon standing, fine red crystals separate. These are then blotted dry with absorbent tissue, dried for a few hours over H_2SO_4 and analysed. The substance transforms rather easily to $Co(NCS)_2 \cdot 3DMSO$ and care and moderation are required in these drying operations in order to obtain a pure sample. (Found: C, 24·58; H, 5·20; Co, 11·80. Calc. for $C_{10}H_{24}N_2S_4O_4Co$; C, 24·43; H, 4·92; Co, 11·99%).

$Co(NCS)_2 \cdot 3DMSO$. $Co(NCS)_2 \cdot 4DMSO$ is readily converted to the deep blue $Co(NCS)_2 \cdot 3DMSO$ on standing in air for a few weeks, on pumping over H_2SO_4 or on pumping at 80°. It may then be recrystallized from acetone. (Found: C, 23·70; H, 4·44; Co, 14·27. Calc. for $C_5H_{18}N_2S_5O_3Co$: C, 23·46; H, 4·43; Co, 14·39%).

$NiBr_2 \cdot 6DMSO$. Two grammes (9·1 mM) of anhydrous nickel bromide are dissolved in 40 g (0·51M) of DMSO while warming to 80°. On cooling the product separates as light green needles. The crystals are carefully dried over sulphuric acid at room temperature. (Found: Ni, 8·54; Br, 23·50; C, 20·60; H, 5·51. Calc. for $C_{12}H_{36}S_6O_6\ NiBr_2$: Ni, 8·54; Br, 23·25; C, 20·97; H, 5·28%). This preparation is difficult to reproduce and the substance is apparently of only marginal stability.

$NiBr_2 \cdot 4DMSO$. On heating $NiBr_2 \cdot 6DMSO$ in vacuum at 61° it is rapidly converted into light blue $NiBr_2 \cdot 4DMSO$. (Found: Ni, 10·82; Br, 29·84; C, 17·83; H, 4·63. Calc. for $C_8H_{24}S_4O_4NiBr_2$: Ni, 11·05, Br, 30·10; C, 18·09; H, 4·56%).

$NiBr_2 \cdot 3DMSO$. Upon prolonged heating in vacuum at 80°, $NiBr_2 \cdot 4DMSO$ is converted into dark green $NiBr_2 \cdot 3DMSO$. (Found: Ni, 12·85; Br, 35·26; C, 16·12; H, 3·87. Calc. for $C_6H_{18}S_3O_3NiBr_2$: Ni, 12·96; Br, 35·29; C, 15·91; H, 4·01%).

$NiI_2 \cdot 6DMSO$. Two grammes (5·9 mM) of anhydrous nickel iodide are dissolved in 40 g (0·51M) of dimethylsulphoxide while heating to 80°. On cooling the red-orange solution the green product crystallizes. The crystals are carefully dried over conc. sulphuric acid at room temperature, but are very unstable with respect to a red compound ($NiI_2 \cdot 4DMSO$, see below) and analyse only approximately as $NiI_2 \cdot 6DMSO$. (Found: Ni, 7·65, 7·69; I, 34·95; C, 13·54, 14·00; H, 4·95, 5·04; Calc. for $C_{12}H_{36}S_6O_6NiI_2$: Ni, 7·51; I, 32·48; C, 18·45; H, 4·64%).

$NiI_2 \cdot 4DMSO$. On standing in air or over calcium choride, $NiI_2 \cdot 6DMSO$ slowly loses DMSO, forming red $NiI_2 \cdot 4DMSO$. The conversion is rapid upon heating in vacuum at 61°. (Found: Ni, 9·40; I, 40·82; C, 15·11; H, 4·03. Calc. for $C_8H_{24}S_4O_4NiI_2$: Ni, 9·39; I, 40·61; C, 15·37; H, 3·87%).

$Ni(NCS)_2 \cdot 4DMSO$. Nickel thiocyanate was prepared as a yellow-brown precipitate by dissolving nickel carbonate in aqueous HNCS (from AgNCS and H_2S), and concentration of the resulting solution. It dissolves readily in DMSO to give a green solution. On removing DMSO by distillation in vacuum at 80° the green solid product separates. (Found: Ni, 11·84; C, 24·86; H, 5·11. Calc. for $C_{10}H_{24}S_6O_4N_2Ni$: Ni, 12·04; C, 24·64; H, 4·96%).

$Ni(NO_3)_2 \cdot 4DMSO$. On pumping down solutions of $Ni(NO_3)_2 \cdot 6H_2O$ in dimethylsulphoxide green glassy materials are obtained. However, a pale green friable solid may be obtained by evaporating such solutions over sulphuric acid in vacuum. (Found: Ni, 11·55; C, 19·60; H, 5·11. Calc. for $Ni(NO_3)_2 \cdot 4DMSO$; Ni, 11·85; C, 19·41; H, 4·85%).

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TABLE 1.—MAGNETIC DATA FOR DMSO COMPLEXES OF COBALT (II)

Compound	χ_M^{corr} (cgsu × 10^6)	Diamagnetic correction (cgsu × 10^6)	Temp. (°K)	μ_{eff}^a (BM)	Notes
$Co(ClO_4)_2 \cdot 6DMSO$	10,460	−347	298	5·02	b
$CoI_2 \cdot 6DMSO$	10,380	−368	298	5·00	c
$Co(NCS)_2 \cdot 4DMSO$	10,060	−260	297	4·96	c
$CoCl_2 \cdot 3DMSO$	9,753	−198	297	4·83	b
	9,827	−198	298	4·86	c
$CoBr_2 \cdot 3DMSO$	9,780	−217	298	4·85	c
$CoI_2 \cdot 3DMSO$	10,480	−253	298	5·02	c
$Co(NCS)_2 \cdot 3DMSO$	9,310	−216	299	4·74	c

(a) Calculated from χ_M^{corr} using the Curie equation, $\mu_{eff} = 2{\cdot}84(\chi_M^{corr}T)^{\frac{1}{2}}$.
(b) Previously reported.[1]
(c) Present work.

TABLE 2.—MAGNETIC DATA FOR DMSO COMPLEXES OF NICKEL (II)

Compound	χ_M^{corr} (cgsu × 10^6)	Diamagnetic correction (cgsu × 10^6)	Temp. (°K)	μ_{eff}^a (BM)	Notes
$Ni(ClO_4)_2 \cdot 6DMSO$	4633	−347	298	3·34	c
	4652	−347	301	3·36	b
$NiI_2 \cdot 4DMSO$	4152	−249	298	3·16	c
$Ni(NCS)_2 \cdot 4DMSO$	4343	−215	298	3·22	c
$NiCl_2 \cdot 3DMSO$	5478	−198	300	3·65	b
$NiBr_2 \cdot 4DMSO$	5948	−262	298	3·78	c
$NiBr_2 \cdot 3DMSO$	5546	−217	299	3·67	c
$Ni(NO_3)_2 \cdot 4DMSO$	4148	−228	297	3·15	c

(a) Calculated from χ_M^{corr} using the Curie equation, $\mu_{eff} = 2{\cdot}84(\chi_M^{corr}T)^{\frac{1}{2}}$.
(b) Previously reported.[1]
(c) Present work.

Magnetic measurements

Bulk susceptibilities were measured with a sensitive Guoy balance by methods previously described.[2-5] Essential data and computed values of the magnetic moments are summarized in Tables 1 and 2.

Spectral measurements

Visible spectra were measured on solids by reflectance using a Beckman DU spectrophotometer with the standard Beckman reflectance attachment with USP $MgCO_3$ as a blank. Infra-red spectra were taken on nujol mulls using a Perkin-Elmer recording infra-red spectrophotometer equipped with a rock salt prism.

Acknowledgement—We thank the U.S. Atomic Energy Commission for financial support under Contract No. AT(30-1)-1965.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 69 to 76. Pergamon Press Ltd.

SOME ESTERS AND CARBOXYLIC ACIDS AS DONOR MOLECULES

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(*Received* 8 *June* 1960)

Abstract—Infra-red spectra of addition compounds of $CH_3COOC_2H_5$ with $SbCl_5$, $SnCl_4$ and $SbCl_3$ and of addition compounds of $HCOOC_2H_5$ with $SnCl_4$ and $SbCl_3$ have been obtained. The shifts in ν(C=O) and ν(C—O) have been studied and it is shown that the carbonyl oxygen atom functions as a donor atom.

Infra-red spectra of the donor–acceptor systems CH_3COOH–$SbCl_5$, CH_3COOH–$SnCl_4$, CH_3COOH–$SbCl_3$ and $HCOOH$–$SbCl_5$ as pure mixtures or as solutions in 1,2-dichlorethane have also been investigated. In those cases ν(C=O) and ν(O—H) have been studied. The spectra indicate that the carbonyl oxygen is the donor atom and that the strong acceptor $SbCl_5$ forms adducts with the monomeric acids, but that in interaction with the weaker acceptors $SnCl_4$ and $SbCl_3$ the hydrogen bonds are retained.

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ADDITION compounds with esters and carboxylic acids as donor molecules and with compounds like $SbCl_5$ and $SnCl_4$ as acceptor molecules were early prepared.[1,2] It has however not been established which of the oxygen atoms functions as donor atom, the carbonyl oxygen atom or the ether oxygen atom.* PFEIFFER[2] has not questioned the donor function of the carbonyl oxygen but BROWN[3] *et al.* have suggested that the ether oxygen is the donor atom in compounds like BF_3.RCOOR′. It must also be taken into account that the same donor molecule may react differently with different acceptor molecules.

This paper deals with an attempt to solve the problem by infra-red spectroscopy. The directions of the shifts in the carbonyl-bond stretching frequencies of the donor molecules after addition of some acceptor molecules are studied.

EXPERIMENTAL

Chemicals. $SbCl_5$ and $SnCl_4$ were purified by distillation at reduced pressure. $SbCl_3$ was purified by sublimation. $CH_3COOC_2H_5$, $HCOOC_2H_5$, CH_3COOH, HCOOH and 1,2-$C_2H_4Cl_2$ were distilled. (b.p. 77°, 54°, 118°, 101° and 84°C). In what follows, the mole ratio of donor D to acceptor A in a compound or mixture is indicated by the fraction following the molecular formulae—thus D:A x:y.

Spectroscopic measurements. The infra-red spectra were recorded on a Perkin-Elmer Model 21 Spectrophotometer equipped with a NaCl prism. The spectra were run with the pure mixtures in thin layers between NaCl plates and the solutions in 1,2-dichlorethane in a 0·05 mm cell.

Ethyl acetate and ethyl formate as donor molecules. A compound $SbCl_5.CH_3COOC_2H_5$ has been reported.[1] It is crystalline at room temperature but is very hygroscopic and cannot be ground in air. It was thus not possible to obtain infra-red spectra of the crystals without extra arrangements to avoid moisture. The compound was soluble, however, in an excess of ethyl acetate and this mixture was studied. The mixtures of $SnCl_4$ and $SbCl_3$ with ethyl acetate are liquid at room temperature. No compounds have been isolated but the spectra indicate donor–acceptor interaction.

* The authors are indebted to the referee for drawing their attention to two recent papers which present evidence of the same type for the donor function of the carbonyl oxygen in esters: (H. F. LAPPERT, paper at International Conference on Co-ordination Chemistry, London, April 1959; abstract (on BX_3-ethyl acetate adducts) published in *Chem. Soc. Spec. Publ.* No 13, p. 179; D. S. BYSTROV and H. N. FILIMONOV, *Dokl. Akad. Nauk*, SSSR **131**, 338 (1960).

[1] A. ROSENHEIM and W. LOEWENSTAMM, *Dtsch. Chem. Ges. Ber.* **35**, 1116 (1902).
[2] P. PFEIFFER, *Liebigs Ann.* **376**, 285 (1910).
[3] H. C. BROWN, H. I. SCHLESINGER and A. B. BURG, *J. Amer. Chem. Soc.* **61**, 673 (1939).

Ethyl formate gave with $SbCl_5$ a very slightly soluble product with high melting point. This product was not further studied. $SnCl_4$:$HCOOC_2H_5$ 1:2 formed as hygroscopic crystals soluble in an excess of ethyl formate. $SbCl_3$:$HCOOC_2H_5$ 1:1 was a liquid at room temperature.

The carbonyl frequencies are situated in formates about 1720 cm^{-1} and in acetates close to 1740 cm^{-1}.[4] Studies of the frequency near 1200 cm^{-1} in formates and near 1250 cm^{-1} in acetates indicate the correlation of those bands with the C—O stretching vibration.[4,5] The spectra of the pure esters and the mixtures are given in Figs. 1 and 2.

The spectra of the mixtures show in all cases decreases in the C=O stretching mode and increases in the C—O stretching mode referred to the spectra of the pure esters.

Because the composition of the mixtures did not correspond to addition compounds there would be no sense in comparing the magnitude of the shifts or in discussing the splitting of the bands.

Acetic acid and formic acid as donor molecules. Addition compounds $SbCl_5.CH_3COOH$[1] and $SbCl_3.CH_3COOH$[6] have been reported. The compound with $SbCl_5$ is crystalline and hygroscopic and was not studied. The compound with $SbCl_3$ is liquid at room temperature. $SnCl_4$ and acetic acid gave two liquid phases at mole ratio 1:1, but at 1:2 they were miscible.

$SbCl_5$ gave hygroscopic crystals with formic acid and $SnCl_4$ gave two very viscous liquid phases which were not studied. $SbCl_3$:HCOOH 1:1 is a viscous liquid.

The carbonyl frequencies are situated in the range 1705–1725 cm^{-1} [4] in saturated carboxylic acids. The spectra of $SnCl_4$:CH_3COOH 1:2 and $SbCl_3$:CH_3COOH 1:1 show a decrease in this frequency referred to the liquid acid. (Fig. 3). $SbCl_3$ did not change the spectrum of the formic acid.

The spectra of carboxylic acids have peaks near 1400 cm^{-1} and 1300 cm^{-1} which are proposed to arise from C—O vibration but coupled with OH in a plane deformation vibration.[7] It is thus not possible to study the C—O stretching vibrations in the acids in the same way as in the esters.

The O—H bond stretching frequency in the pure acids has a broad shape typical of hydrogen bonded OH-groups.[8] This shape is altered gradually and the center of the absorption shifts to higher frequencies. However there is no sharp peak indicating free OH-groups. (Fig. 3).

The compounds with $SbCl_5$ and the acids were soluble in 1,2-dichlorethane. Spectra of such solutions (10 mole per cent) were obtained and for comparison also solutions of the earlier studied liquids. (Figs. 4 and 5. The frequencies given by WILMSHURST[9,10] for the monomeric acids are indicated at the bottom in the figures). The range about 2950 cm^{-1} where the solvent absorbs is excluded in the figures. (Unfortunately neither the crystals with $SbCl_5$ nor the liquids with $SnCl_4$ and $SbCl_3$ were soluble in CCl_4).

In the spectra of the adducts with $SbCl_5$, the C=O band is split and the lower frequencies show a decrease referred to the polymeric acid. All shifts are negative referred to the monomeric acids. The main peak in the O—H region is in both cases sharp and situated near the frequencies for the monomeric acids. It thus seems as if the hydrogen bonds are almost completely broken in the adduct formation. (The shoulders about 2500 cm^{-1} however may indicate a very weak association).

The solution of $SnCl_4$:CH_3COOH 1:2 in 1,2-dichlorethane gave about the same spectrum as the pure liquid mixture.

The small shift in the C=O stretching mode obtained with $SbCl_3$ in acetic acid is not to be seen in the solution in 1,2-dichlorethane, but there is still a small shift in the O—H stretching mode.

DISCUSSION

The shifts in the carbonyl bond stretching frequency in addition compounds with ketones[11–13] and aldehydes[14] and different acceptor molecules have been studied

[4] L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*. John Wiley, London, New York (1954).
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[7] C. G. PIMENTEL and A. L. MCCLELLAN, *The Hydrogen Bond*, p. 122. Freeman & Co., San Francisco; London (1960).
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[12] M. ZACKRISSON and K. I. ALDÉN, *Acta Chem. Scand.* **14**, 994 (1960).
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[14] L. PAOLONI and G. B. MARINI-BETTÒLO, *Gazz. Chim. Ital.* **89**, 1972 (1959).

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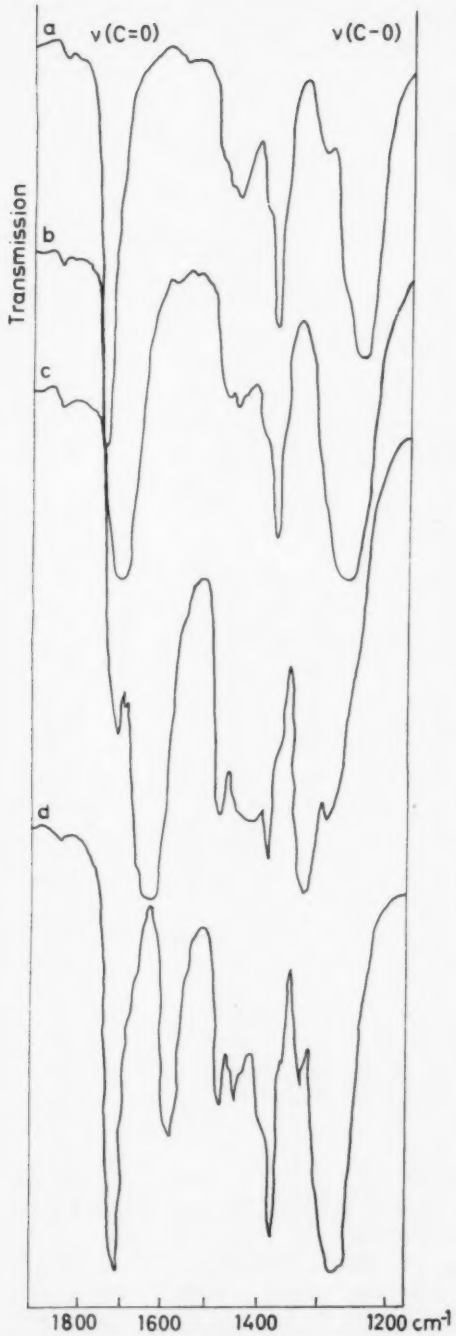

FIG. 1.—Infra-red spectra in the range 5–8·5 μ of: (a) $CH_3COOC_2H_5$, (b) $SbCl_3$: $CH_3COOC_2H_5$ 1:2, (c) $SnCl_4$: $CH_3COOC_2H_5$ 1:2, (d) $SbCl_5$: $CH_3COOC_2H_5$ 1:2.

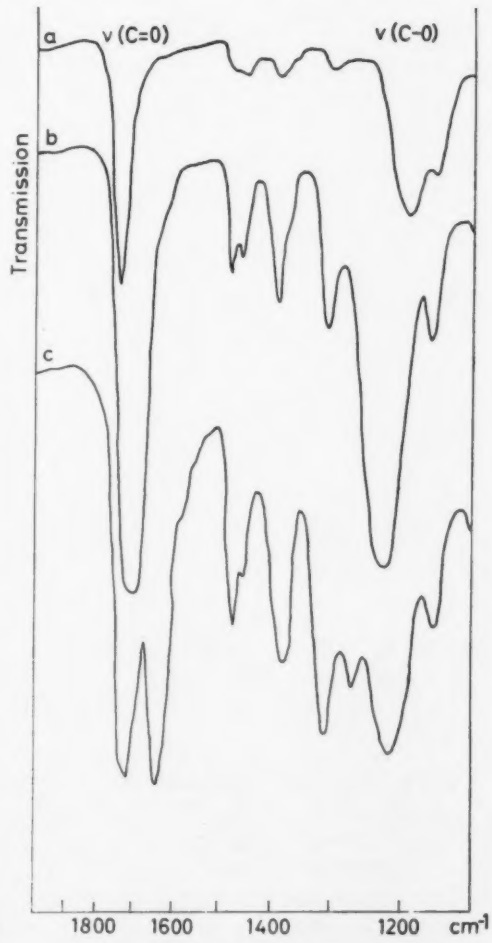

FIG. 2.—Infra-red spectra in the range 5–9 μ of: (a) $HCOOC_2H_5$, (b) $SbCl_3$: $HCOOC_2H_5$ 1:1, (c) $SnCl_4$: $HCOOC_2H_5$ 1:4.

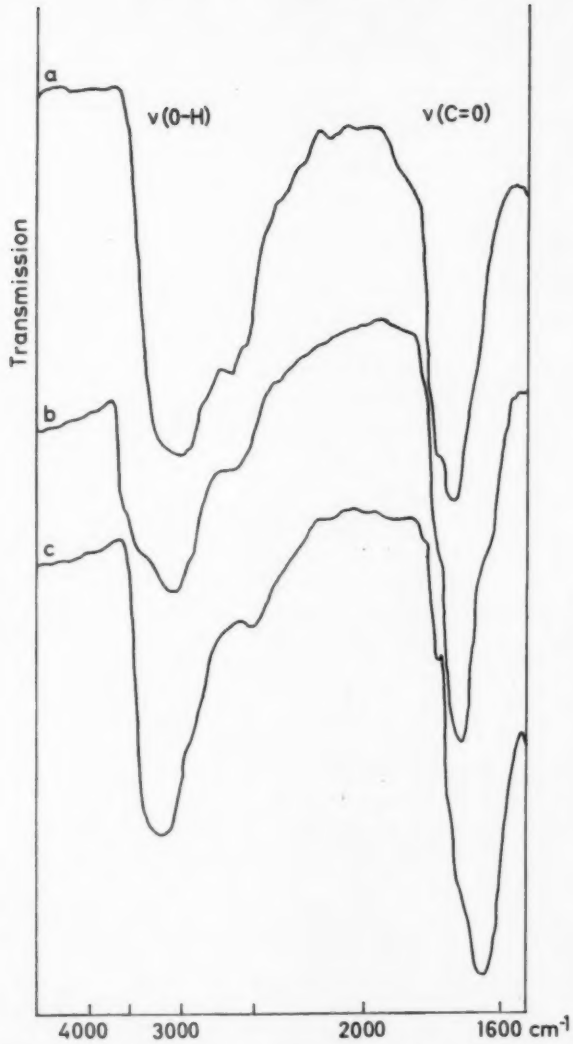

FIG. 3.—Infra-red spectra in the range 2–6·5 μ of: (a) CH_3COOH, (b) $SbCl_3$:CH_3COOH 1:1; (c) $SnCl_4$:CH_3COOH 1:2.

earlier by infra-red spectroscopy. In those cases the adduct formation has always caused negative shifts. The same effect has been shown by Raman spectroscopy for hydrogen bond formation with alcohols and phenols.[15–17]

In the hydrogen bond formation with esters, the decrease in frequency for the C═O stretching mode is accompanied by an increase for the C—O stretching mode.[15] These two effects are analogous to the decrease in the P—O bond frequency and the

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[16] G. P. PURANIK, *Proc. Indian. Acad. Sci.* **37** A 499 (1959).
[17] G. P. PURANIK, *Proc. Indian. Acad. Sci.* **38** A 233 (1953).

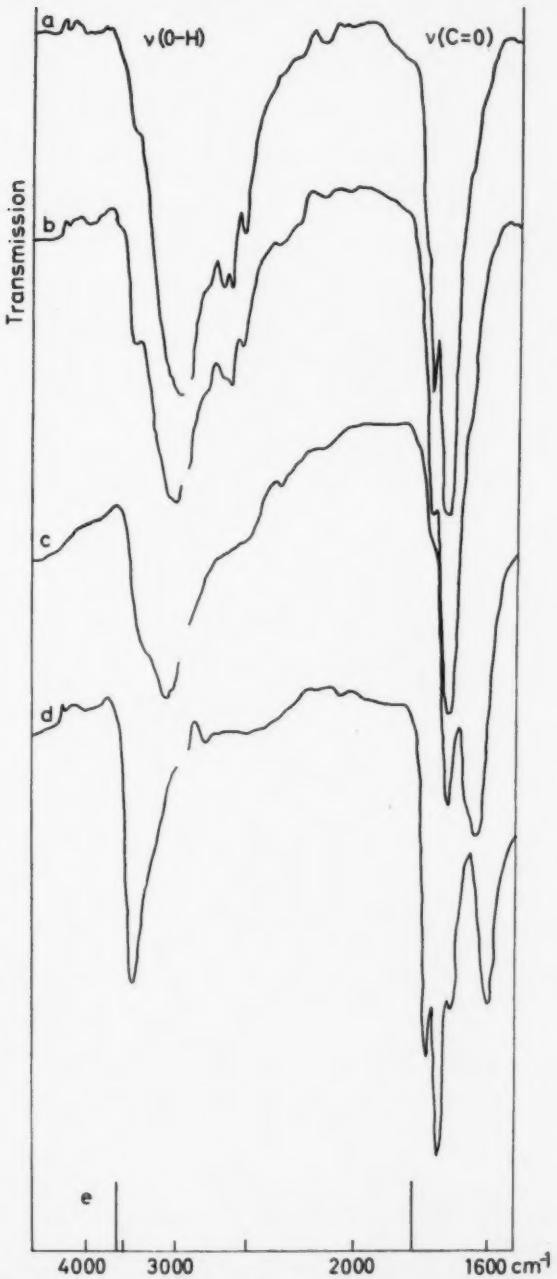

FIG. 4.—Infra-red spectra in the range 2–6·5 μ of solutions in 1,2-dichlorethane (10 mole per cent) of: (a) CH_3COOH, (b) $SbCl_3$:CH_3COOH 1:1, (c) $SnCl_4$:CH_3COOH $\frac{1}{2}$:1, (d) $SbCl_5$:CH_3COOH 1:1, (e) Frequencies of monomeric CH_3COOH given by WILMSHURST[9].

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increase in the P—Cl bond frequencies found in $POCl_3$ due to interaction with acceptor molecules.[18]

If the carbonyl oxygen atom of an ester is the donor atom, a decrease in the C═O

FIG. 5.—Infra-red spectra in the range 2–6·5 μ of solutions in 1,2-dichlorethane (10 mole per cent) of: (a) HCOOH, (b) $SbCl_5$:HCOOH 1:1, (c) Frequencies of monomeric HCOOH given by WILMSHURST[19].

stretching mode can thus be expected, possibly accompanied by an increase in the C—O stretching mode.

If the ether oxygen atom is the donor atom, the formation of an adduct should cause electron withdrawal from the carbon atom in the C═O bond. It can be assumed that the donor-acceptor interaction in this case should have the same effect on the

[19] P.-O. KINELL, I. LINDQVIST and M. ZACKRISSON, *Acta Chem. Scand.* **13**, 1159 (1959).

C=O bond frequency as a substitution of a more electronegative CF_3-group for a CH_3-group in the alcohol residue of the ester. It has been shown that such a substitution is followed by an increase in the C=O stretching mode. The actual frequencies are for example 1739 cm^{-1} in $C_3H_7COOC_2H_5$ and 1767 cm^{-1} in $C_3H_7COOCH_2CF_3$.[19]

In adduct formation, electrons are withdrawn first from the donor atom and as a secondary effect from the adjacent atom. According to a description of inductive effects on chemical bonds recently published,[20] a weakening of a bond can usually be expected when electrons are withdrawn from the most electronegative atom of the bond and a strengthening when electrons are withdrawn from the least electronegative atom.

If the carbonyl oxygen of an ester is the donor atom, a weakening of the C=O bond thus can be expected and as a secondary effect a strengthening of the adjacent C—O bond, in the spectra indicated as a decrease in the C=O stretching mode and an increase in the C—O stretching mode. Opposite shifts could be expected if the ether oxygen atom is the donor atom.

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The results presented here, the decrease in the C=O stretching mode and the increase in the C—O stretching mode, clearly indicate that, with the acceptor molecules studied, the carbonyl oxygen in the esters is the donor atom. This conclusion is thus based both upon analogy with earlier experiments and upon the discussion of inductive effects on chemical bonds.

The discussion of the effects found with the acids is complicated by the existence of intermolecular hydrogen bonds. Chains of molecules are shown to be present in liquid formic acid, but the structure of liquid acetic acid is not clarified.[21] The spectra of the acids in the concentrated solutions in 1,2-dichlorethane show that hydrogen bonds are still present, but it is not important whether the molecules are chains or cyclic dimers, as in the gaseous state. The negative shifts in the C=O stretching mode show that the carbonyl oxygen is the donor atom in the acids too.

The withdrawal of electrons from the carbonyl oxygen in adduct formation ought to weaken the hydrogen bond to this atom and to strengthen the adjacent O—H bond of the system O . . . . H—O.[20] This effect should be more obvious in interaction with strong acceptor molecules. The small shifts with $SbCl_3$, earlier known as a weak acceptor molecule,[12,18] indicate also in this case very weak interaction. $SnCl_4$ as a stronger acceptor give larger shifts which remained even at dilution with a solvent. The spectra, however, still indicate association with hydrogen bonds. $SbCl_5$, evidently the strongest acceptor studied here, causes such a strong interaction that the hydrogen bonds are broken. It thus seems as if $SbCl_5$ forms an adduct mainly with a monomeric acid, while the weaker acceptor molecules form adducts mainly with the dimeric or polymeric acid.

HASSEL *et al.* have found that the oxygen in acetone forms two bonds with the very weak acceptor molecule Br_2[22] and that in the compound $2CH_3OH.Br_2$ both hydrogen bridges and halogen bridges to the same oxygen atom are present.[23] It is suggested

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[22] O. HASSEL and K. O. STRØMME, *Acta Chem. Scand.* **13**, 275 (1959).
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that this is possible because of the two lone pair electrons available on the oxygen atom. Our results support such a suggestion provided that the bonds are not too strong.

It is of course possible that the solid compounds should give other results and spectroscopic studies of solid compounds and particularly structure determinations would be of great interest.

Acknowledgement—A grant from the Swedish Natural Science Research Council is gratefully acknowledged.

We wish to thank Professor G. HÄGG for all facilities put at our disposal and Mr. S. JOHANSSON for helpful assistance.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 77 to 83. Pergamon Press Ltd.

METAL CARBONYLS—II[1]

CARBON MONOXIDE AND CHLORIDE EXCHANGE WITH SOME CYCLOPENTADIENYL METAL CARBONYLS*†

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(*Received* 8 *July* 1960)

Abstract—The exchange reactions of ^{14}CO with cyclopentadienyl metal carbonyls in solution have been studied. The nickel and cobalt cyclopentadienyl carbonyls exchange rapidly whereas the other compounds equilibrate very slowly. The exchange in $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$ depends on the carbon monoxide concentration and hence proceeds by a bimolecular displacement. The rates and mechanism are discussed and possible explanations are presented in terms of electronic structures, steric hindrance and M—CO bond strengths. It is suggested that the results may provide some evidence in support of certain electronic differences between metals in the simple carbonyls and those in the "isoelectronic" cyclopentadienyl carbonyls. The chloride exchange with $C_5H_5Fe(CO)_2Cl$ in 5 per cent ethanol–water is second-order in the complex and independent of the chloride ion concentration. The reaction is very slow in benzene. An attempt is made to correlate the CO and chloride exchange results.

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THE kinetics and mechanism of carbon monoxide exchange with nickel tetracarbonyl and dicobalt octacarbonyl[1,2] have been reported recently. It was observed that the exchange proceeds by dissociation and is very rapid at 25°. On the other hand, the simplest metal carbonyls of iron, manganese, and chromium exchange extremely slowly under the same conditions. The primary purpose of the study reported herein was to extend this investigation to cyclopentadienyl metal carbonyls.

Although little is known about reaction mechanisms of simple metal carbonyls, even less information is available on cyclopentadienyl metal carbonyls. Moreover, it is of interest to compare the reactions of these two classes of compounds with regard to the presumed electronic structures of the metals. Since all of the cyclopentadienyl π-electrons are believed to participate to some extent in the bonding of the metal,[3,4] the latter in a broad general sense attains an "inert gas configuration". Thus metals of at. no. n in simple carbonyls and metals of at. no. $n + 1$ in cyclopentadienyl carbonyls, *viz.*, $Co_2(CO)_8$ and $(C_5H_5)_2Ni_2(CO)_2$, also $Fe(CO)_5$ and $C_5H_5Co(CO)_2$, may be considered as isoelectronic. Because of this analogy it was of interest to compare rates and mechanism of CO exchange in such "isoelectronic" systems.

* This research was supported in part by a Research Corporation Grant-in-Aid.

† Based upon a portion of the dissertation presented to Northwestern University by A. WOJCICKI, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1960. Part of this work was presented as paper no. 139 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

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EXPERIMENTAL

Materials. The compound $(C_5H_5)_2Ni_2(CO)_2$ was prepared by the method of FISCHER and PALM[5], $(C_5H_5)_2Fe_2(CO)_4$ and $C_5H_5Fe(CO)_2Cl$ by the method of PIPER *et al.*[6] All three were purified and identified by analyses and/or infra-red spectra. Other compounds were generously supplied as follows: $C_5H_5Co(CO)_2$ and $(C_5H_5)_2Mo_2(CO)_6$ by Dr. H. W. STERNBERG of the U.S. Bureau of Mines, $C_5H_5Mn(CO)_3$ and $CH_3C_5H_4Mn(CO)_3$ by Dr. T. H. COFFIELD of the Ethyl Corporation, $C_5H_5V(CO)_4$ by Professor E. O. FISCHER of the University of Munich, and $CH_3C_6H_5Cr(CO)_3$ by Dr. M. C. WHITING of Oxford University.

All solvents were purified, except 95 per cent ethanol, which was used directly. Pure toluene, free from sulphur compounds, was obtained using the method described by FIESER[7]. Thiophene-free benzene was refluxed over sodium for several hours and then fractionally distilled. Chlorobenzene was dried over Drierite and distilled. Distilled water was used for the chloride exchange experiments.

Carbon monoxide of C.P. grade, obtained from Matheson Co., was passed through concentrated sulphuric acid prior to use. Carbon-14 monoxide (1·0 mc, 54·3 ml), purchased from Tracerlab, Inc., was transferred to a 2 l. storage flask, diluted to 1 atm with inactive CO, and used in this form. Argon from Matheson Co. was also dried with H_2SO_4.

Chlorine-36 hydrochloric acid was obtained from the AEC as a concentrated aqueous solution and was subsequently diluted with water. n-Octadecylbenzyldimethylammonium chloride* was obtained from Rohm and Haas Co. The inactive compound was tagged with radio-chloride using the method described by PEARSON *et al.*[8] Reagent grade potassium nitrate was used.

Determination of the rate of carbon monoxide exchange. The apparatus used and the experimental procedure for determining CO exchange in cyclopentadienyl metal carbonyls was the same as that described in some detail earlier.[1] Briefly, the method involved measuring the rate of decrease of radioactivity in a closed system at constant temperature, starting with gaseous radio-carbon monoxide and inactive metal carbonyl solution. The exchanges were run at 1 atm, the partial pressure of CO having been varied by dilution with Ar. With fast reactions, the gas was continuously circulated through the solution; with slow reactions, where the rate of diffusion is rapid compared to the rate of exchange, no circulatory pump was used. Solutions were carefully protected from light and the infra-red spectra were determined at the end of each run to establish whether or not any chemical decomposition of the cyclopentadienyl metal carbonyl had taken place. Duplicate kinetic runs were made with a 10 per cent precision.

All of the exchange reactions investigated were found to follow the MCKAY[9] equation and give linear plots of $\log [A_0 - A_\infty/A - A_\infty]$ vs. time, where A_0 is the initial radioactivity in the gas phase, A is the radioactivity at time t, and A_∞ is the equilibrium radioactivity. The slope of these lines equals $k_{apparent}/2{\cdot}303$, which is related to k_{true} by the equation

$$k_{true} = k_{apparent} \frac{Xa^{1-\alpha} y\, b^{1-\beta}}{Xa + y\, b} \tag{1}$$

where a is the concentration of cyclopentadienyl metal carbonyl, α is the order in a, b is the concentration of carbon monoxide, β is the order in b, y is the ratio of moles of CO in solution to those in the whole system, and X is the number of exchangeable CO's in the carbonyl. The kinetic plots (Fig. 1) show an apparent negative fraction exchange at zero-time, instead of passing through the origin. This shift arises from the treatment of the experimental data. During the initial 30 min, equilibration between the CO dissolved in solution and the ^{14}CO in the gas phase leads to a rapid decrease in radioactivity. To overcome this difficulty the zero-time activity, A_0, used was that measured after 30 min.

Determination of the rate of chloride exchange. Separate solutions of $C_5H_5Fe(CO)_2Cl$ and of $R_4N^{36}Cl$ or $H^{36}Cl$ were prepared in the solvent to be used. These solutions were mixed and thermostatted at 25·1°. Aliquots of 0·20 ml were removed at known intervals and the uncomplexed chloride

* Henceforth referred to as R_4NCl.

[5] E. O. FISCHER and C. PALM, *Ber. Dtsch. Chem. Ges.* **91**, 1725 (1958). We wish to thank Professor E. O. FISCHER for the gift of a sample of $(C_5H_5)_2Ni$.
[6] T. S. PIPER, F. A. COTTON and G. WILKINSON, *J. Inorg. Nucl. Chem.* **1**, 165 (1955).
[7] L. F. FIESER, *Experiments in Organic Chemistry*, p. 364. D. C. Heath and Company, New York (1941).
[8] R. G. PEARSON, H. B. GRAY and F. BASOLO, *J. Amer. Chem. Soc.* **82**, 787 (1960).
[9] H. A. C. MCKAY, *Nature, Lond.* **142**, 997 (1938).

was precipitated by adding 30 per cent excess of the required aqueous or alcoholic silver nitrate solution. The mixture was centrifuged for 4 min and then an aliquot of the clear supernatant liquid was withdrawn and evaporated on a disk of filter paper in an aluminium tray under strong infra-red light. The activity of all these samples was then counted in a Scaling Unit, Model 182A, Nuclear Instruments and Chemical Corporation, Inc. The data were analysed as described for the CO exchange experiments.

RESULTS

Qualitative results for carbon monoxide exchange with cyclopentadienyl metal carbonyls are given in Table 1. Of the compounds investigated, only $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$ exchange rapidly enough for a detailed kinetic study. Despite

TABLE 1.—RATES OF CO EXCHANGE WITH CYCLOPENTADIENYL AND ARENE METAL CARBONYLS

Metal carbonyl	Concentration (mmole/l.)		Solvent	Temp (°C)	Exchange
	Carbonyl	$(CO)_s$***			
$(C_5H_5)_2Ni_2(CO)_2$	21–23	0·7–6	Toluene	25	fast*
$C_5H_5Co(CO)_2$	26	8	Toluene	0	v. fast*
$(C_5H_5)_2Fe_2(CO)_4$	24	0·5	Chlorobenzene	32	slow†
$C_5H_5Mn(CO)_3$	45	6	Toluene	32	v. slow‡
$CH_3C_5H_4Mn(CO)_3$	66	6	Toluene	32	v. slow‡
$(C_5H_5)_2Mo_2(CO)_6$	22	6	Toluene	32	v. slow‡
$CH_3C_6H_5Cr(CO)_3$	45	5	Toluene	25	v. slow‡
$C_5H_5V(CO)_4$	23	6	Toluene	25	v. slow‡,**

* For specific rates, see Tables 2 and 3.
† Solution decomposes slowly. Very slight exchange observed in 4 days.
‡ No detectable exchange in 3 weeks.
** Extreme caution is necessary in handling solutions of $C_5H_5V(CO)_4$. Presence of even small traces of air and/or moisture leads to an apparent exchange through decomposition.
*** Conc. of dissolved CO.

special precautions taken, $(C_5H_5)_2Fe_2(CO)_4$ decomposes slowly under the experimental conditions. Kinetic plots for the exchange of $C_5H_5Co(CO)_2$ in toluene as a function of CO concentration are shown in Fig. 1. Data on the exchange of $(C_5H_5)_2Ni_2(CO)_2$ are reported in Table 2, on $C_5H_5Co(CO)_2$ in Table 3. The chloride exchange data for $C_5H_5Fe(CO)_2Cl$ in 5 per cent ethanol–water and benzene solutions are shown in Table 4.

DISCUSSION

The exchange of radiocarbon monoxide with cyclopentadienyl metal carbonyls follows the same trend as that with the simplest first row transition metal carbonyls. The nickel and cobalt compounds, $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$, exchange much faster than the other cyclopentadienyl metal carbonyls investigated, i.e., $(C_5H_5)_2Fe_2(CO)_4$, $C_5H_5Mn(CO)_3$, $(C_5H_5)_2Mo_2(CO)_6$, and $C_5H_5V(CO)_4$. The qualitative agreement between the two classes of metal carbonyls with respect to their CO exchange stops however at this point. Whereas the exchange in $Ni(CO)_4$ and $Co_2(CO)_8$ were shown to proceed by a dissociative path, the data for $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$ (Tables 2 and 3) clearly indicate first-order dependence on the carbon

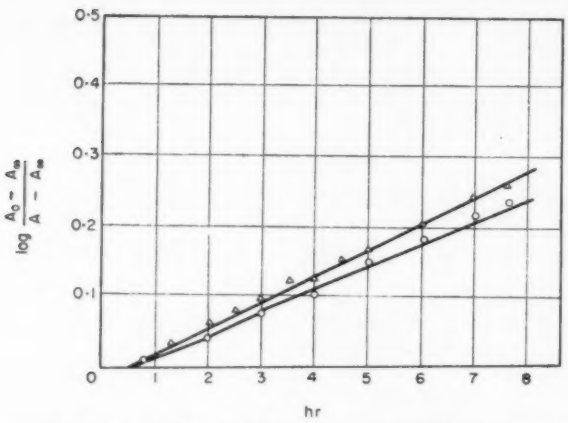

FIG. 1.—Rates of exchange of CO with a 25·5 mmole/l. toluene solution of $C_5H_5Co(CO)_2$ at −33·4°C as a function of CO concentration. Concentrations of CO in mmoles/l. are: —O—, 2·1, and —Δ—, 8·5.

TABLE 2.—RATES OF CO EXCHANGE WITH $(C_5H_5)_2Ni_2(CO)_2$ IN TOLUENE*

Concentration (mmole/l.)		$(CO)_t$††	Temp (°C)	$k_{apparent}$ ($sec^{-1} \times 10^4$)	k_{true} ($l.mole^{-1}\,sec^{-1} \times 10^3$)†
$(C_5H_5)_2Ni_2(CO)_2$	$(CO)_s$**				
22·9	6·2	6·2	25·0	2·0	5·3
20·6	2·8	1·1	25·0	1·8	6·1
22·3	0·66	0·25	25·0	1·6	6·6
24·5	7·6	2·8	0	0·15	0·27

* $E_a \sim 20$ kcal/mole
† Rate $= k[(C_5H_5)_2Ni_2(CO)_2][CO]$
** Conc. of dissolved CO
†† Total mmoles of CO in the enclosed system

TABLE 3.—RATES OF CO EXCHANGE WITH $C_5H_5Co(CO)_2$ IN TOLUENE*

Concentration (mmole/l.)		$(CO)_t$**	Temp (°C)	$k_{apparent}$ ($sec^{-1} \times 10^5$)	k_{true} ($l.mole^{-1}\,sec^{-1} \times 10^4$)†
$C_5H_5Co(CO)_2$	$(CO)_s$**				
25·5	7·6	2·7	0	130	220
25·5	7·8	2·7	−12	35	57
25·5	8·5	3·0	−33·4	2·3	4·1
25·5	2·1	0·62	−33·4	2·0	4·9

* $E_a = 16$ kcal/mole
† Rate $= k[(C_5H_5Co(CO)_2][CO]$
** Conc. of dissolved CO

TABLE 4.—RATE OF CHLORIDE EXCHANGE WITH $C_5H_5Fe(CO)_2Cl$ AT 25·1°C

Source of $^{36}Cl^-$	Concentration (mmole/l.)			Solvent	$k_{apparent}$ ($sec^{-1} \times 10^6$)	k_{true} ($l.mole^{-1}$ $sec^{-1} \times 10^3$)*
	$C_5H_5Fe(CO)_2Cl$	Cl^-	KNO_3			
HCl	2·55	2·55	—	5%C_2H_5OH—H_2O	6·42	1·26
HCl	1·27	2·55	—	5%C_2H_5OH—H_2O	2·34	1·23
HCl	5·10	2·55	—	5%C_2H_5OH—H_2O	16·6	1·09
HCl	2·55	2·55	100	5%C_2H_5OH—H_2O	10·0	1·97
HCl	2·55	1·27	100	5%C_2H_5OH—H_2O	16·9	2·21
R_4NCl	2·55	2·55†	—	Benzene	v. slow‡	—

* Rate = $k[C_5H_5Fe(CO)_2Cl]^2$
† Concentration of R_4NCl
‡ No detectable exchange in 3 days.

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monoxide concentration. Thus a bimolecular, S_N2, mechanism is proposed for the latter reactions.

It has been suggested[1] that a dissociative mechanism for the exchange in $Ni(CO)_4$ may result from the absence of vacant low energy orbitals on the nickel. This and the presence of the filled 3*d* orbitals should render nucleophilic attack of carbon monoxide energetically unfavourable and thus lead to dissociation. In cyclopentadienyl metal carbonyls, the nature of the bonding between carbon monoxide and the metal is essentially similar to that in simple metal carbonyls.[3,4] The only difference between the two classes of compounds is a partial replacement of carbon monoxide by the π-cyclopentadienyl ring. Thus any difference in lability and/or mechanism of exchange may perhaps be accounted for in terms of electronic changes resulting from such a replacement.

In terms of the simple valence bond treatment of cyclopentadienyl metal carbonyls, the cyclopentadienyl ring is essentially a tridentate ligand, the metal being in the +1 oxidation state. All of the π-electrons from the ring interact with vacant 3*d*, 4*s*, and 4*p* orbitals of the metal thus resulting in an inert gas configuration of the latter. Therefore, according to this theory, the metals in $(C_5H_5)_2Ni_2(CO)_2$ and $Co_2(CO)_8$, as also in $C_5H_5Co(CO)_2$ and $Fe(CO)_5$, are isoelectronic. Such an approach immediately causes some concern in explaining the CO exchange results. Whereas both $Co_2(CO)_8$ and $(C_5H_5)_2Ni_2(CO)_2$ exchange rapidly, the former reacts by dissociation and the latter by a nucleophilic displacement. Even a more striking difference is observed with "isoelectronic" $C_5H_5Co(CO)_2$ and $Fe(CO)_5$. The cobalt compound exchanges very rapidly and by an S_N2 path, the iron compound extremely slowly by an unknown mechanism. These two sets of results are difficult to interpret if one assumes identical electronic structures for the metals.

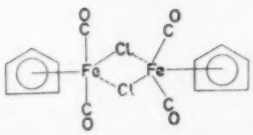
The results can be explained more readily on the basis of the molecular orbital theory. Thus all all low-lying metal orbitals, i.e., 3*d*, 4*s*, and 4*p*, make some contribution to the bonding, but the extent of their participation varies somewhat from one compound to another. This then gives rise to empty anti-bonding orbitals which may be of lower energy and hence more readily accessible to the attacking nucleophile than are the corresponding orbitals in the simple metal carbonyls. Immaterial of the electronic structure of the activated complex, the important conclusion that the CO

experiments point to is that metal atoms in simple metal carbonyls and those in the corresponding cyclopentadienyl compounds do not appear to be isoelectronic in the true sense of the word. Thus the results support the view that the "inert gas" rule is merely a useful formalism for the prediction of new compounds but it does not always explain their reactivities.

The lability trend shown in Table 1 can be explained on the basis of a bimolecular mechanism proposed for these compounds. Unfortunately, no quantitative theoretical calculations are available for the bonding in cyclopentadienyl metal carbonyls, so it is possible to offer only a reasonable qualitative explanation. In going from $C_5H_5Co(CO)_2$ to $C_5H_5V(CO)_4$ along the first transition series, the number of carbon monoxide groups increases thus rendering the central metal ion sterically less accessible. Although such an explanation is plausible, it may deal only with a secondary effect. It is possible that with an increase in the coordination number of the metal, the energy of its lowest available vacant orbital also increases. Finally, the relative strength of the M—CO bond may also be an important factor. It has been shown that the Cr—CO and Fe—CO bonds in the respective carbonyls are stronger than the Ni—CO bond in $Ni(CO)_4$.[10] Should this trend also hold for M—CO bonds in cyclopentadienyl metal carbonyls, then a possible explanation for lack of lability in higher-co-ordinated cyclopentadienyl carbonyls may be sought in terms of the relative bond strengths. In order to evaluate the importance of each of these contributing factors, more thermodynamic and spectroscopic work is required.

In addition to the above-mentioned reactions with cyclopentadienyl metal carbonyls, the exchange was also carried out with $CH_3C_6H_5Cr(CO)_3$. Although no quantitative treatment of the bonding in arene metal carbonyls is as yet available, these compounds may be compared to the corresponding cyclopentadienyls. Adopting such an approach, it is not surprising that $CH_3C_6H_5Cr(CO)_3$ shows no apparent exchange with CO, as neither $C_5H_5Mn(CO)_3$ nor $CH_3C_5H_4Mn(CO)_3$ equilibrates under the same conditions.

In view of the experimental findings for the $(C_5H_5)_2Ni_2(CO)_2$ and $C_5H_5Co(CO)_2$ exchanges with ^{14}CO, it was of interest to determine whether or not cyclopentadienyl metal carbonyls undergo other substitution reactions by a bimolecular mechanism. The exchange reaction of chloride ion with $C_5H_5Fe(CO)_2Cl$ has been selected for this purpose. Unfortunately, the exchange proceeds very slowly in benzene and therefore the ethanol–water mixed-solvent was used for a detailed study. The data in Table 4 show that the exchange is independent of the chloride ion concentration but depends on the second power of the $C_5H_5Fe(CO)_2Cl$ concentration. The nature of the solvent used prevents a clear-cut mechanistic interpretation. However, it is possible that the activated complex undergoing exchange may have the structure in which a low energy



vacant iron orbital interacts with a filled orbital on a "foreign" co-ordinated chlorine. The solvent may then assist in the removal of the ligand. That the solvent does play a

[10] F. A. COTTON, A. K. FISCHER and G. WILKINSON, *J. Amer. Chem. Soc.* **81**, 800 (1959).

significant role is shown by the fact that the exchange, although very slow in benzene, is rapid in ethanol–water. Whether this is caused by the greater solvation energy in ethanol-water due to hydrogen bonding, or by the nucleophilic solvent displacement of the chloride, or whether both contribute, is not known. Clearly, the exact nature of the activated carbonyl complex cannot be assigned on the basis of the available kinetic data.

Acknowledgement—We wish to thank the Eastman Kodak Company for providing a fellowship to A. W.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 84 to 87. Pergamon Press Ltd.

A SOLID COMPLEX OF TETRAETHYLENEPENTAMINE

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(*Received* 12 *July* 1960; *revised* 24 *August* 1960).

Abstract—The preparation of stable, crystalline nitro(tetraethylenepentamine)-cobalt(III) perchlorate and three other salts of the same cation are reported. Physical and chemical evidence is cited to support the formula [Co tetren(NO_2)]$^{2+}$ for the cation in which all five amine nitrogens are co-ordinated to the same cobalt ion. Resolution into optical antipodes has not been possible using standard procedures.

THERE has recently been some interest in the higher polyethyleneamines* as co-ordinating ligands, both from the point of view of the solution stability of their complexes[1–4] and the composition and stereochemistry of their complexes.[5–10] The interest in the stability of the complexes toward dissociation in aqueous solution and the determination of stability constants has been aimed on the one hand at the analytical application[2,3] of the polyamines for metal analyses by titration and on the other hand at extending the so-called "chelate effect".[11] Since the preparation of several *trien* complexes of Co(III) by BASOLO[6] in 1948, there have been *trien* complexes reported for Ni(II)[5a,7,12], Pd(II) and Pt(II)[6b]. Resolution of blue-violet [Co trien Cl_2]$^+$ into optical isomers was reported by DAS SARMA and BAILAR[9a] proving its *cis*-configuration and most recently SELBIN and BAILAR[9b] have reported the isolation of both *cis* and *trans* [Co trien Br_2]$^+$, demonstrating that the *trien* molecule can co-ordinate with its four nitrogens lying in the same plane, but that this configuration must be forced.

There are very few reports of complexes containing *tetren*. JONASSEN and FREY[7] reported a 1:1 and a 2:1 complex between Co(II) and *tetren*, based upon a spectrophotometric study. They isolated several solid Co(II) complexes[7,8] which they formulated as [Co tetren H_2O] $(ClO_4)_2$, [Co tetren (CH_3OH)]X_2 (X = Cl or ClO_4), [Co tetren (CH_3OH)][$CoCl_4$] and [Co tetren $(OH)]_2$[Pt Cl_6]. Their assumption that the Co(II) is octahedrally co-ordinated and that all five polyamine nitrogens are bound to the metal is probably correct, although there is no substantial proof offered to support these assumptions. The only other report in the literature of a solid

* Triethylenetetramine (trien) and tetraethylenepentamine (tetren).

[1] H. B. JONASSEN and L. WESTERMAN, *J. Amer. Chem. Soc.* **79**, 4275 (1957).
[2] C. N. REILLEY and R. W. SCHMID, *J. Elisha Mitchell sci. Soc.* **73**, 279 (1957).
[3] C. N. REILLEY and J. H. HOLLOWAY, *J. Amer. Chem. Soc.* **80**, 2917 (1958).
[4] B. KIRSON, *Bull. Soc. Chim. France*, 1178 (1957).
[5] H. B. JONASSEN and B. E. DOUGLAS, *J. Amer. Chem. Soc.* **71**, 4094 (1949); H. B. JONASSEN and N. L. CULL, *Ibid.* **71**, 4097 (1949).
[6] F. BASOLO, *J. Amer. Chem. Soc.* **70**, 2634 (1948).
[7] H. B. JONASSEN and F. W. FREY, *J. Amer. Chem. Soc.* **75**, 1524 (1953).
[8] H. B. JONASSEN and F. W. FREY, *J. Amer. Chem. Soc.* **79**, 2454 (1957).
[9] B. DAS SARMA and J. C. BAILAR, JR., *J. Amer. Chem. Soc.* **77**, 5480 (1955); J. SELBIN and J. C. BAILAR, JR., *Ibid.*, **82**, 1524 (1960).
[10] C. K. JORGENSEN, *Acta Chem. Scand.* **11**, 399 (1957).
[11] A. MARTELL and M. CALVIN, *Chemistry of the Metal Chelate Compounds*, p. 145. Prentice-Hall, New York (1953).
[12] R. G. PEARSON, C. R. BOSTON and F. BASOLO, *J. Phys. Chem.* **59**, 304 (1955).

tetren complex is the admittedly impure [Co tetren Cl]Cl_2 prepared by PEARSON, *et al.*[12], during the course of their studies on mechanisms of substitution reactions of Co(III) complexes. REILLEY and HOLLOWAY[3] have reported the stability constants for the *tetren* complexes of Hg^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+} and Mn^{2+}, but no mention was made of any attempt to isolate solid complexes.

The preparation and characterization of a very stable yellow crystalline complex with the composition [Co tetren NO_2]$(ClO_4)_2$ is reported here. Evidence that all five nitrogens of the pentamine are co-ordinated is also presented.

EXPERIMENTAL

A. *Preparation of compounds*[13]

1. [Co tetren (NO_2)] $(ClO_4)_2$. (a) $Na_3[Co(NO_2)_6]$ (40·4 g, 0·10 mole) was dissolved in 100 ml water and *tetren* (18·0 g, 0·095 mole) added. The resulting brown solution was refluxed 8 hours, filtered, and an excess of concentrated $HClO_4$ added slowly. The solution was evaporated in an air stream until orange hexagonal crystals began forming. After cooling in ice, the first batch of crystals was removed by filtration, washed with alcohol and ether. Recrystallization was effected from water heated to 65°C and containing a drop of $HClO_4$. Further evaporation of the original filtrate yielded a second crop of crystals. Total yield of crude [Co tetren (NO_2)]$(ClO_4)_2$:34 g. or 72% based on the *tetren*. (Found: C, 19·41; H, 4·81; N, 16·98; ClO_4, 40·7. Calc. for [Co tetren (NO)]$(ClO_4)_2$: C, 19·48; H, 4·70; N, 17·04; ClO_4, 40·3%).

(b) A mixture containing $Co(NO_3)_2 \cdot 6H_2O$ (10·0 g, 0·0343 mole), *tetren* (6·5 g, 0·0343 mole), HNO_3 (1·08 g, 0·0172 mole) and $NaNO_2$ (4·72 g, 0·0684 mole) in 75 ml of water, was air-oxidized for 8 hr. The solution was filtered and the filtrate evaporated to half its volume. $HClO_4$ was added dropwise and crystals formed immediately. These were filtered, washed with alcohol and ether, and air-dried. A second crop of crystals was obtained as before. Yield: 8·7 g or 51 per cent based on *tetren*. (Found: C, 20·00; H, 5·21; N, 16·44; ClO_4, 40·4. Calc. for [Co tetren (NO_2)]$(ClO_4)_2$: C, 19·48; H, 4·70; N, 17·04; ClO_4, 40·3%).

2. *Other salts.* The following three compounds, all containing the new complex cation, were obtained as crystalline solids by mixing solutions of the complex cation with solutions of the appropriate complex anions.

(a) Red-orange—[Co tetren (NO_2)] $[Cr(NH_3)_2(NCS)_4]_2$ Found: N, 26·9. Calc. for [Co tetren (NO_2)] $[Cr(NH_3)_2(NCS)_4]_2$: N, 27·11%).

(b) Dark yellow—[Co tetren (NO_2)] $[PtCl_4]$ Found: Cl, 22·3; Pt, 30·85. Calcd. for [Co tetren (NO_2)] $[PtCl_4]$: Cl, 22·47; Pt, 30·91%).

(c) Bright yellow—[Co tetren (NO_2)] $[AuCl_4]_2$ (Found: Cl, 29·2; Au, 40·5. Calc. for [Co tetren (NO_2)] $[AuCl_4]_2$: Cl, 29·19; Au, 40·54%).

No compounds could be obtained by ordinary metathesis reactions with the following anions: $PtCl_6^{2-}$, $Ni(CN)_4^{2-}$, $Co(NH_3)_2(NO_2)_4^-$, Cr ox_3^{3-} (ox = oxalate), CrO_4^{2-}, $Cr_2O_7^{2-}$, PO_4^{3-}, $PdCl_4^{2-}$, NO_3^-, SO_4^{2-}, Cl^-, Br^-, I^-. No reaction occurred when a solution of the complex was heated with salicylaldehyde.

B. *Attempts to resolve the cation,* [Co tetren (NO_2)]$^{2+}$

A saturated solution of [Co tetren (NO_2)] $(ClO_4)_2$ was divided into nine fractions and the following nine solid resolving agents were added separately in small portions to the nine solutions;

(1) ammonium D-α-bromocamphor-π-sulphonate
(2) potassium D-camphorsulphonate
(3) D-tartaric acid
(4) potassium D-antimonyltartrate
(5) sodium D-camphornitronate
(6) sodium dibenzoyl-D-tartrate
(7) diacetyl D-tartaric anhydride
(8) L-malic acid
(9) D-α-aminophenylacetic acid

[13] J. SELBIN, Thesis, University of Illinois (1957).

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Even after the solutions had become saturated with resolving agent, none of the diastereoisomers crystallized out. (In the cases of 1, 2 and 4, NH_4ClO_4 or $KClO_4$ was obtained.)

C. *Physical measurements*

1. Visible and ultra-violet spectra were obtained with a Cary Model 15 Recording Spectrophotometer.

2. Infra-red spectra were obtained with a Perkin-Elmer Model 21 Recording Spectrophotometer. The KBr pellet method was used and samples checked in Nujol.

3. Polarographic data were obtained using a Sargent Model 21 Recording Polarograph.

RESULTS AND DISCUSSION

The yellow-orange, non-hygroscopic crystals of [Co tetren NO_2]$(ClO_4)_2$ are soluble in water, producing a yellow solution having a visible and ultra-violet spectrum quite similar to the nitropentammine complex:

	λ_1	log ε	λ_2	log ε	λ_3	log ε
[Co $(NH_3)_5$ NO_2]Cl_2[14]	457·5	2·34	325	3·23	239	4·05
[Co tetren NO_2]$(ClO_4)_2$	460	2·35	328	3·26	243	4·59
[Co trien $(NO_2)_2$]ClO_4[13]	437	2·34	323	3·66	244	4·40

The dinitrotriethylenetetramine cobalt(III) complex is included for comparison. The complex in aqueous solution undergoes acid hydrolysis at a very slow rate at room temperature, but base hydrolysis (e.g. in 0·1 M NaOH) occurs visibly within minutes, the yellow solution becoming red, characteristic colour of the Co(III)–oxygen bond. Heating neutral solutions of the complex at 100°C for 5–10 min causes visible aquation. No crystalline salts were isolated of either the aqua- or hydroxo-complex, although this was not attempted using any of the large and unusual anions which gave solids with the nitro cation.

Evidence that all five of the polyamine nitrogens are co-ordinated to the cobalt comes from several sources besides the yellow colour of the compound which is characteristic of Co(III) complexes with six nitrogen donors. Aqueous solutions of the complex are slightly acidic and show no tendency to react with strong acids or with salicylaldehyde as would be the case if there were a free amine group. All Co(III) complexes are six-co-ordinate and the infra-red spectrum of the compound reveals no water bands, eliminating this species as a possible ligand. No free amine absorption is found and as the following bands for the co-ordinated nitro group (in cm^{-1}) show, the latter is co-ordinated as —NO_2 and not —ONO. The cation [Co trien $(NO_2)_2$]$^+$ is again included for comparison purposes since its infra-red spectrum has not

	ν_1 (sym)	ν_2 (bend)	ν_3 (asym)
[Co en_2Y NO_2]$^{2+}$[15]	1323 ± 12	822 ± 4	1414 ± 13
[Co$(NH_3)_5ONO$]$^{2+}$[16]	1065	528	1468
[Co$(NH_3)_5NO_2$]$^{2+}$[16]	1310	824	1428
[Co tetren NO_2]$^{2+}$	1317, 1308	822	1425, 1416
[Co trien$(NO_2)_2$]$^{+}$[13]	1315, 1304	820	1425, 1418

[14] R. C. BRASTED and C. HIRAYAMA, *J. Phys. Chem.* **63**, 780 (1959).
[15] J. CHATT, *et al.*, *J. Chem. Soc.* 4073 (1959).
[16] K. NAKAMOTO, J. FUJITA and H. MURATA, *J. Amer. Chem. Soc.* **80**, 4817 (1958).

previously been published. For both the latter compound and the *tetren* complex the symmetric and the asymmetric stretching frequencies are split.

Although the new complex cation can theoretically exist in four different geometrical arrangements, each asymmetric and potentially optically active, no success was achieved in either separating geometrical isomers or resolving optical isomers. Nor is it known which of the four geometrical arrangements has been obtained.

Polarographic results are of interest since it might be supposed that the large multidentate chelating agent would strongly stabilize the complex ion toward reduction. However, as the following results[13] show, this is not the case. It is seen that

Complex	0·1 M electrolyte	$-E_{\frac{1}{2}}$ vs S.C.E.
cis-$[Co(NH_3)_4(NO_2)_2]NO_3$	$HClO_4$	0·023
	$NaNO_3$	0·022
trans-$[Co(NH_3)_4(NO_2)_2]NO_3$	$HClO_4$	0·18
	$NaNO_3$	0·18
cis-$[Co\ en_2(NO_2)_2]NO_3$	$HClO_4$	0·20
	$NaNO_3$	0·25
trans-$[Co\ en_2(NO_2)_2]NO_3$	$HClO_4$	0·24
	$NaNO_3$	0·27
$[Co\ trien(NO_2)_2]NO_3$	$HClO_4$	0·23
	$NaClO_4$	0·225
$[Co\ tetren(NO_2)](ClO_4)_2$	$HClO_4$	0·145
	$NaClO_4$	0·29

neither *trien* nor *tetren* confer any added stability upon the Co(III), in fact they even will allow more ready reduction to Co(II), pointing up the greater stability of Co(II) complexes when multidentate rather than unidentate groups are present. It is perhaps significant in this connection that the second reduction wave (for Co(II) to Co(O)Hg), which ordinarily occurs at about −1·29 V (vs S.C.E.) for most cobalt complexes, is shifted to considerably more negative potential in the *trien* and *tetren* complexes.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 88 to 97. Pergamon Press Ltd.

PHASE EQUILIBRIA IN THE SYSTEM CsF–ThF_4

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(*Received* 10 *May* 1960; *in revised form* 7 *July* 1960)

Abstract—The phase equilibrium diagram of the condensed system CsF–ThF_4 has been constructed from a combination of results obtained using both thermal analysis and quenching techniques. Phase identification was accomplished by petrographic and X-ray diffraction analysis. In the system CsF–ThF_4 seven compounds have been identified. Three of these, $3CsF{\cdot}ThF_4$, $2CsF{\cdot}ThF_4$ and $CsF{\cdot}ThF_4$, melt congruently at 980°, 869° and 839°, respectively. The compounds $2CsF{\cdot}3ThF_4$, $CsF{\cdot}2ThF_4$, and $CsF{\cdot}6ThF_4$ melt incongruently at 842°, 860° and at 1010°, respectively. The compound $CsF{\cdot}2ThF_4$ decomposes on cooling to $2CsF{\cdot}3ThF_4$ and $CsF{\cdot}3ThF_4$ at 813°. The compound $CsF{\cdot}3ThF_4$ has a subsolidus upper limit of stability at 830°. None of the compounds occurring in the system has been described previously. Comparisons of the phase equilibria in the system CsF–ThF_4 are made with those of other binary systems of ThF_4 and alkali fluorides.

ALTHOUGH many detailed studies of the phase equilibria in binary and ternary fluoride fused salt systems have been made within the last ten years[1] no previous reports have appeared concerning the phase equilibria in the system CsF–ThF_4. Phase diagrams have been constructed for each of the binary systems of the quadrivalent fluorides ZrF_4 and UF_4 with the alkali fluorides,[1] and for the binary systems of ThF_4 with LiF,[2] NaF,[2,4] KF,[3,4] and RbF.[5] It was, therefore, of interest that a study of the phase equilibria in the system CsF–ThF_4 be made as a means of affording a better understanding of the interactions in condensed salt systems.

Molten salt systems containing ThF_4 are of significance in the selections of nuclear reactor breeder or converter fuels which utilize ThF_4 as a fertile material for the production of fissionable ^{233}U. Solutions of UF_4 and ThF_4 in ^7LiF–BeF_2 or in NaF–BeF_2 solvent mixtures have been proposed as fuels for such converters.[6] As cesium, one of the common fission products, becomes a component of an operating nuclear reactor, using a fluoride fused salt fuel, a knowledge of the phase relationships involving CsF and ThF_4 may be necessary in devising operational and reprocessing procedures.

EXPERIMENTAL

Materials

The mixtures used in these phase equilibrium studies were prepared from reagent grade cesium fluoride and thorium fluoride. No impurities in the reagents were observed by X-ray diffraction and microscopic analysis (using the polarizing light microscope). Less than 0·2 weight per cent impurities

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† Operated for the United States Atomic Energy Commission by the Union Carbide Corporation.

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in thorium fluoride were found by spectroscopic analysis. In cesium fluoride the following impurities were determined by spectroscopic analysis: Ca: 0·2, K: 0·15, Li: 0·001, Na: 0·5, Rb: 1·0%.

The phase equilibrium data were obtained by thermal analysis of slowly cooled melts and by identifying phases present in mixtures which were equilibrated and quenched. Because the cesium fluoride reagent contained approximately one weight per cent water, it was pre-dried at 135° before it was used in any weight measurements involving preparation of materials for phase studies. Thorium fluoride is easily converted to oxyfluoride or oxide at elevated temperatures[7] and because cesium fluoride is extremely hygroscopic, it was necessary to remove small amounts of water and oxygen as completely as possible from starting materials. To facilitate further removal of these substances, ammonium bifluoride was added to the mixtures of $CsF–ThF_4$ before initial heating in the thermal analysis experiments. The oxides were converted by the reaction with ammonium bifluoride to products which have not been identified but which are believed to be ammonium fluometallates.[8] Upon further heating, the ammonium metallates decomposed to form metal fluorides. The same mixtures were used later for quenching experiments. In order to prevent reformation of oxides or hydrates after the ammonium bifluoride was removed, the mixtures were melted and cooled under a dry helium atmosphere. The grinding of slowly cooled melts, preparatory to loading tubes for quenching experiments, was performed in an argon atmosphere dry-box. The only time when the cooled melts were exposed to air after removal of the ammonium bifluoride occurred in a short period during a transfer from the furnace to a dry-box. During this short period only the mixtures which contained a large fraction of CsF were observed to take up water.

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Apparatus and methods

The techniques used for measurement of the temperatures which define the $CsF–ThF_4$ phase diagram as well as the X-ray and microscopic techniques used in identifying phases have been discussed previously.[9–11] The accuracy of the temperature measurements reported in these studies is limited by the characteristics of the chromel-alumel thermocouples used. Manufacturers estimate this accuracy to be within 5° in the temperature range 400–800°. The accuracy and precision of the determinations reported here are considered to be within this limit of error. The uncertainty in temperatures shown in Table 3 indicates the temperature differences between adjacent quenched samples from which the values were obtained.

DISCUSSION OF RESULTS

No previous reports are known concerning either the phase equilibria in the system $CsF–ThF_4$ or existence of $CsF–ThF_4$ compounds. The phase equilibrium diagram reported here (Fig. 1) represents a synthesis from thermal analysis and thermal gradient quenching data. In association with seven $CsF–ThF_4$ compounds there occur four eutectic and three peritectic invariant points. The invariant equilibria for this system are listed in Table 1. Results of thermal analysis and thermal gradient quenching experiments are given in Tables 2 and 3. In regions of fluoride systems where several stable compounds occur within a relatively small composition area, it frequently occurs that reproducible equilibrium data from cooling curves cannot be obtained. In such instances, the data derived from observations of the phases present in samples which have been quenched from a state of phase equilibrium serve to elucidate the phase relationships in a system. The phase diagram of the system $CsF–ThF_4$ at concentrations of ThF_4 greater than 50 mole per cent was established principally from identification of phases present in such quenched samples. Formulas for the three congruently melting $CsF–ThF_4$ compounds were established by the fact that almost

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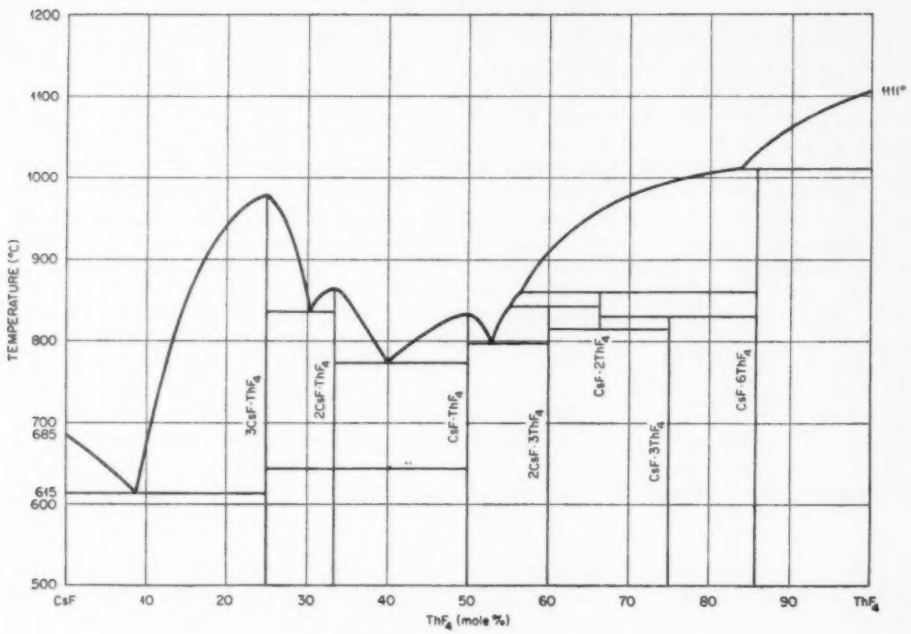

FIG. 1.—The system $CsF–ThF_4$.

TABLE 1.—INVARIANT EQUILIBRIA IN THE SYSTEM $CsF–ThF_4$

Mole % ThF_4 in liquid	Invariant temperature (°C)	Type of equilibrium	Phase reaction at invariant temperature
9	615	Eutectic	$L \rightleftharpoons CsF + 3CsF{\cdot}ThF_4$*
25	980	Congruent melting point	$L \rightleftharpoons 3CsF{\cdot}ThF_4$
30·5	838	Eutectic	$L \rightleftharpoons 3CsF{\cdot}ThF_4 + 2CsF{\cdot}ThF_4$
33·3	869	Congruent melting point	$L \rightleftharpoons 2CsF{\cdot}ThF_4$
40	775	Eutectic	$L \rightleftharpoons 2CsF{\cdot}ThF_4 + CsF{\cdot}ThF_4$
50	839	Congruent melting point	$L \rightleftharpoons CsF{\cdot}ThF_4$
53	797	Eutectic	$L \rightleftharpoons CsF{\cdot}ThF_4 + 2CsF{\cdot}3ThF_4$
55	842	Peritectic	$L + CsF{\cdot}2ThF_4 \rightleftharpoons 2CsF{\cdot}3ThF_4$
56·5	860	Peritectic	$L + CsF{\cdot}6ThF_4 \rightleftharpoons CsF{\cdot}2ThF_4$
—	813	Lower limit of stability of $CsF{\cdot}2ThF_4$	$CsF{\cdot}2ThF_4 \rightleftharpoons 2CsF{\cdot}3ThF_4 + CsF{\cdot}3ThF_4$
75	830	Upper limit of stability of $CsF{\cdot}3ThF_4$	$CsF{\cdot}2ThF_4 + CsF{\cdot}6ThF_4 \rightleftharpoons CsF{\cdot}3ThF_4$
84	1010	Peritectic	$L + ThF_4 \rightleftharpoons CsF{\cdot}6ThF_4$

* "L" refers to liquid

TABLE 2.—THERMAL EFFECTS OCCURRING DURING THE COOLING OF $CsF–ThF_4$ MIXTURES

Composition (mole %)		Liquidus temperature (°C)	Solidus temperature (°C)	Other thermal effects (°C)
CsF	ThF_4			
96	4	648	615	
94	6	637	615	
92	8	621	617	
90	10	690	618	
83·7	16·7	895	602	
75	25	981	—	
70	30	872	—	
66·7	33·3	869	—	645
60	40	—	782	647
53·8	46·2	820	773	648
50	50	838	—	661
45	55	864	—	830, 656
40	60	907	—	859
37·5	62·5	941	—	861
33·3	66·7	981	860	—
29	71	1022	—	857
25	75	1035	—	847
20	80	843	—	

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pure single phase material was found in both slowly cooled and quenched samples of mixtures containing 25, 33·3 and 50 mole % ThF_4. Formulas for the three incongruently melting compounds and the sub-solidus compound $CsF·3ThF_4$ were established by the fact that almost pure single-phase material was observed in quenched samples of mixtures containing 60, 66·7, and 85·7 mole % ThF_4, which were heated to temperatures just below the solidus, or at the $CsF·3ThF_4$ compound composition, just below the upper temperature of stability, for sufficient time to achieve equilibrium.

The phrase "almost pure single-phase material" is used here in view of the fact that very rarely does a solid phase at nominal compound composition appear to be absolutely free of traces of a second phase, because it is fortuitous that components can be weighed so precisely that an *exact* design composition will be produced. Occasional checks on the composition of mixtures show that these normally fall within $\pm 0·5$ mole per cent of design composition. It is usual, therefore, that traces of impurity can be detected using the petrographic microscope which do not appear in X-ray diffraction patterns. Absolutely pure single-phase material observed routinely at nominal compound compositions usually indicates solid solution rather than experimental precision in sample preparation. Thus, the phrase "almost pure single-phase material" here also denotes the absence of detectable solid solutions in the binary system.

The length of time required to establish equilibrium at high temperatures depended upon the composition of the sample. Fifty to one-hundred hours was generally a sufficiently long annealing time for equilibrium to be established at temperatures just below the incongruent melting points, and below the upper stability temperature of the compound $CsF·3ThF_4$.

Optical properties and X-ray diffraction data for $CsF–ThF_4$ compounds are listed

TABLE 3.—DATA OBTAINED BY QUENCHING CsF–ThF_4 MIXTURES*

Composition (Mole % ThF_4)	Phase change temp. (°C)	Phases found just above phase change	Phases found just below phase change
10	667 ± 4	L†	$3CsF{\cdot}ThF_4 + L$
16·7	897 ± 3	L	$3CsF{\cdot}ThF_4 + L$
20	944 ± 4	L	$3CsF{\cdot}ThF_4 + L$
30	867 ± 5	L	$3CsF{\cdot}ThF_4 + L$
30	839 ± 6	$3CsF{\cdot}ThF_4 + L$	$3CsF{\cdot}ThF_4 + 2CsF{\cdot}ThF_4$
33·3	868 ± 3	L	β-$2CsF{\cdot}ThF_4$
40	775 ± 4	L	β-$2CsF{\cdot}ThF + CsF{\cdot}ThF_4$
46·2	813 ± 4	L	$CsF{\cdot}ThF_4 + L$
50	839 ± 3	L	$CsF{\cdot}ThF_4$
55	848 ± 3	L	$2CsF{\cdot}3ThF_4 + L$
55	799 ± 4	$2CsF{\cdot}3ThF_4 + L$	$2CsF{\cdot}3ThF_4 + CsF{\cdot}ThF_4$
60	910 ± 3	L	$CsF{\cdot}6ThF_4 + L$
60	864 ± 4	$CsF{\cdot}6ThF_4 + L$	$CsF{\cdot}2ThF_4 + L$
60	847 ± 4	$CsF{\cdot}2ThF_4 + L$	$2CsF{\cdot}3ThF_4$
62·5	931 ± 3	L	$CsF{\cdot}6ThF_4 + L$
62·5	856 ± 5	$CsF{\cdot}6ThF_4 + L$	$CsF{\cdot}2ThF_4 + L$
62·5	847 ± 5	$CsF{\cdot}2ThF_4 + L$	$2CsF{\cdot}3ThF_4 + CsF{\cdot}2ThF_4$
62·5	812 ± 5	$2CsF{\cdot}3ThF_4 + CsF{\cdot}2ThF_4$	$2CsF{\cdot}3ThF_4 + CsF{\cdot}3ThF_4$
66·7	854 ± 5	$CsF{\cdot}6ThF_4 + L$	$CsF{\cdot}2ThF_4$
66·7	810 ± 5	$CsF{\cdot}2ThF_4$	$2CsF{\cdot}3ThF_4 + CsF{\cdot}3ThF_4$
66·7	860 ± 3	$CsF{\cdot}6ThF_4 + L$	$CsF{\cdot}2ThF_4$
66·7	815 ± 4	$CsF{\cdot}2ThF_4$	$2CsF{\cdot}3ThF_4 + CsF{\cdot}3ThF_4$
71	865 ± 3	$CsF{\cdot}6ThF_4 + L$	$CsF{\cdot}2ThF_4 + CsF{\cdot}6ThF_4$
71	832 ± 5	$CsF{\cdot}2ThF_4 + CsF{\cdot}6ThF_4$	$CsF{\cdot}2ThF_4 + CsF{\cdot}3ThF_4$
75	997 ± 4	L	$CsF{\cdot}6ThF_4 + L$
75	869 + 3	$CsF{\cdot}6ThF_4 + L$	$CsF{\cdot}2ThF_4 + CsF{\cdot}6ThF_4$
75	833 ± 4	$CsF{\cdot}2ThF_4 + CsF{\cdot}6ThF_4$	$CsF{\cdot}3ThF_4$
80	832 ± 5	$CsF{\cdot}2ThF_4 + CsF{\cdot}6ThF_4$	$CsF{\cdot}3ThF_4 + CsF{\cdot}6ThF_4$
85·7	1030 ± 6	L	$L + ThF_4$
85·7	1006 ± 7	$L + ThF_4$	$CsF{\cdot}6ThF_4$
95	1084 ± 4	L	$L + ThF_4$

* The uncertainty in temperatures shown in column 2 indicates the temperature differences between the quenched samples from which the values were obtained.

† The symbol "L" refers to liquid (observed as glass or quench growth).

in Table 4. A determination of the crystal parameters of $3CsF \cdot ThF_4$ from X-ray powder patterns shows that this compound is cubic with a cell edge of 9·659 Å.

The occurrence of a reproducible thermal effect at 645° in compositions between 25 and 50 mole % ThF_4 and the fact that the compound $2CsF{\cdot}ThF_4$ was observed only as a poorly-crystallized, highly-twinned material, indicates that $2CsF{\cdot}ThF_4$ exists in two equilibrium crystal forms in the temperature range of this study, i.e., between 400° and the liquidus. The phase, β-$2CsF{\cdot}ThF_4$, reported here, is the lower temperature form, stable only below 645°. The high temperature form, stable above 645°, inverts so rapidly that it is not preserved in the quenching act.

No compounds other than $2CsF{\cdot}ThF_4$ and $CsF{\cdot}ThF_4$ were observed between the compositions 33·3 and 50 mole % ThF_4. Compounds of the general formula, $7MF{\cdot}6XF_4$, where M is an alkali metal cation and X is Zr, Hf, Th, or U, have not

TABLE 4.—OPTICAL PROPERTIES AND X-RAY DATA FOR $CsF–ThF_4$ COMPOUND

$3CsF·ThF_4$

Optical Properties: Isotropic, r.i. = 1·464

Crystal Structure: Simple cubic, $a_0 = 9·659$ Å

β-$2CsF·ThF_4$

Optical Properties: Highly twinned crystals, biaxial, $N_\alpha = 1·500$, $N_\gamma = 1·506$

X-ray data:

d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
6·32	30	2·396	8	1·779	5
4·97	5	2·342	5	1·757	8
4·06	5	2·285	15	1·725	8
3·67	100	2·112	60	1·596	2
3·34	20	2·034	10	1·549	2
3·17	5	1·975	5	1·489	2
2·957	5	1·947	2	1·449	5
2·910	5	1·905	2	1·431	5
2·467	5	1·829	10		

$CsF·ThF_4$

Optical Properties: Highly twinned crystals, biaxial (−), 2V ~ 20°, $N_\alpha = 1·528$,

X-ray data: [$N_\gamma = 1·544$

d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
7·37	55	3·11	5	2·026	15
4·53	5	2·919	3	1·829	10
4·06	7	2·868	9	1·776	10
3·70	60	2·434	5	1·757	10
3·67	100	2·263	10	1·550	5
3·56	85	2·106	20		
3·31	10	2·056	10		

$2CsF·3ThF_4$

Optical properties: Biaxial (+), $2V \sim 15°$, $N_\alpha = 1·518$, $N_\gamma = 1·526$

X-ray data:

d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
7·31	2	3·23	2	2·120	5
6·15	15	2·96	2	2·097	5
4·31	2	2·938	3	2·038	2
4·08	2	2·302	4	1·854	2
3·70	100	2·157	2	1·843	15

$CsF·2ThF_4$

Optical properties: Uniaxial (−), $N_\omega = 1·532$, $N_\epsilon = 1·524$

X-ray data:

d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
5·66	20	2·986	20	2·069	15
3·86	45	2·803	5	1·840	45
3·76	100	2·252	25		

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TABLE 4. (*contd.*)

$CsF{\cdot}3ThF_4$

Optical properties: Biaxial (+), $2V \sim 35°$, $N_\alpha = 1{\cdot}554$, $N_\gamma = 1{\cdot}558$

X-ray data:

d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
8·18	25	3·34	75	2·074	30
7·34	20	3·21	35	2·047	55
4·69	25	2·98	45	2·000	55
4·33	20	2·769	15	1·928	10
4·10	15	2·696	20	1·910	15
3·83	35	2·649	10	1·897	35
3·76	50	2·466	10	1·850	15
3·61	100	2·210	10	1·746	20
3·48	90	2·149	20	1·763	25
3·42	35	2·088	50	1·627	10
				1·560	10

$CsF{\cdot}6ThF_4$

Optical properties: Uniaxial (−), $N_\omega = 1{\cdot}540$, $N_\varepsilon = 1{\cdot}534$

X-ray data:

d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
10.85	10	3·36	10	2·336	5
7·25	10	3·14	10	2·111	55
6·98	10	3·04	10	2·087	60
4·78	10	2·971	20	2·074	25
4·45	10	2·947	20	2·004	10
4·23	100	2·816	15	1·939	10
3·59	60	2·561	5	1·868	30
3·54	45	2·510	10	1·799	10
3·48	15	2·405	5		

been observed in this or in other binary systems where the cation radius ratio M^+/X^{4+} exceeds 1·65.

In the system $CsF–ThF_4$, six of the seven compound formula ratios are identical to those of equilibrium compounds in the system $RbF–UF_4$. Indeed, the close resemblance of the X-ray powder patterns of corresponding phases indicates that the compound pairs are isostructural. The cation radius ratios, M^+/X^{4+} of the pairs Na^+/Zr^{4+} and Na^+/Hf^{4+} are nearly identical and, as expected, the systems contain several pairs of isostructural compounds whose unit cells parameters are nearly identical. The cation radius ratios of Cs^+/Th^{4+} and K^+/Zr^{4+} are considerably closer than those of Cs^+/Th^{4+} and Rb^+/U^{4+}, and yet the compounds in the system $CsF–ThF_4$ bear considerably more resemblance to those of $RbF–UF_4$ than to those of $KF–ZrF_4$. It has been shown[12] that at the beginning of the actinide series the comparable binding energy of the 5*f*-, 6*d*- and 7*p*-levels is a favourable condition for the use of these orbitals in hybridized bonds. It is, therefore, not surprising that analogous isostructural compounds are formed in the systems $RbF–UF_4$ and $CsF–ThF_4$ although not in the system $KF–ZrF_4$.

[12] J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements*, p. 466. John Wiley, New York (1957).

COMPARISONS AMONG SYSTEMS OF ALKALI FLUORIDES WITH THORIUM FLUORIDE

A complete series of phase diagrams of the binary systems formed by the alkali fluorides (excluding Francium) and a second component have been published previously only with the compound BeF_2. The construction of the $CsF–ThF_4$ phase equilibrium diagram now makes possible the comparisons among the binary systems of the alkali fluorides with ThF_4.

As is common in binary systems of alkali fluorides with MF_2, MF_3 or MF_4 com-

TABLE 5.—MELTING TEMPERATURE OF ALKALI FLUORIDE–THORIUM FLUORIDE COMPOUNDS

Compound formula MF/ThF_4	LiF	NaF	KF	RbF	CsF
5 : 1	—	—	712	—	—
4 : 1	—	645	—	—	—
3 : 1	573	—	865	974	980
2 : 1	—	705	747	835	869
3 : 2	—	712	—	—	—
7 : 6	597	*	905	852	—
1 : 1	—	730	—	—	839
2 : 3	—	—	—	—	842
1 : 2	762	831	930	—	860
1 : 3	—	—	990	1004	†
1 : 4	897	—	—	—	—
1 : 6	—	—	—	992	1010

* Metastable
† Subsolidus at its composition

pounds, the composition of the first invariant point in the ThF_4 systems occurs at greater alkali fluoride concentration as the atomic number of the alkali metal cation increases; the melting points of the 3 : 1 compounds increase similarly. NOVOSELOVA[13] attributes the continuous increase of thermal stability, observed as increasing melting point temperatures, of the compounds $2MF·BeF_2$, to an increase of the electronegativity difference between the Be^{2+} ion and that of the alkali metal in the Li to Rb interval, followed by a slight decrease with $2CsF·BeF_2$. In the series alkali fluorides-thorium fluoride, analogous increase of melting point occurs for the $3MF·ThF_4$compounds where they exist (Table 5), while the maximum temperature the eutectic of lowest ThF_4 concentration occurs in the system $KF–ThF_4$. Very similar systematic relationships have been noted at this laboratory in the systems of alkali fluorides with ZrF_4 and with UF_4.

No evidence has been reported for the existence of the compound $3NaF·ThF_4$, nor has it been observed in the studies of the ternary systems $NaF–ZrF_4–ThF_4$,[14] $NaF–ThF_4–UF_4$,[14] or $NaF–BeF_2–ThF_4$.[15] The absence of $3NaF·ThF_4$ does not in itself mean that this compound is less stable than the other $3MF·ThF_4$ compounds, since the system $NaF–ThF_4$ is also the only one in this series which contains the

[13] A. V. NOVOSELOVA, *Uspekhi Khimii* **28**, 33 (1959).
[14] R. E. THOMA, (Editor) ORNL–2548 (1959).
[15] C. F. WEAVER, R. E. THOMA, H. A. FRIEDMAN, and H. INSLEY, Paper presented at the 138th Meeting of the American Chemical Society, New York, New York, 11–16 September (1960).

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neighbouring compound $4MF{\cdot}ThF_4$. Relative stabilities can be assigned to several 3 : 1 compounds only if the adjacent are of the same MF/ThF_4 ratio in each system. This condition is met only in the $RbF–ThF_4$ and $CsF–ThF_4$ systems, where $3CsF{\cdot}ThF_4$ is seen to be more stable than $3RbF{\cdot}ThF_4$, since the latter decomposes into MF and $2MF{\cdot}ThF_4$, whereas the former does not.

Compounds of the unusual formula ratio $7MF{\cdot}6ThF_4$ occur throughout the series of binary systems except in $CsF–ThF_4$. But for $7NaF{\cdot}6ThF_4$, these are equilibrium phases in the systems. Previous discussion has shown that there is a systematic relationship in the occurrence of these compounds.[16]

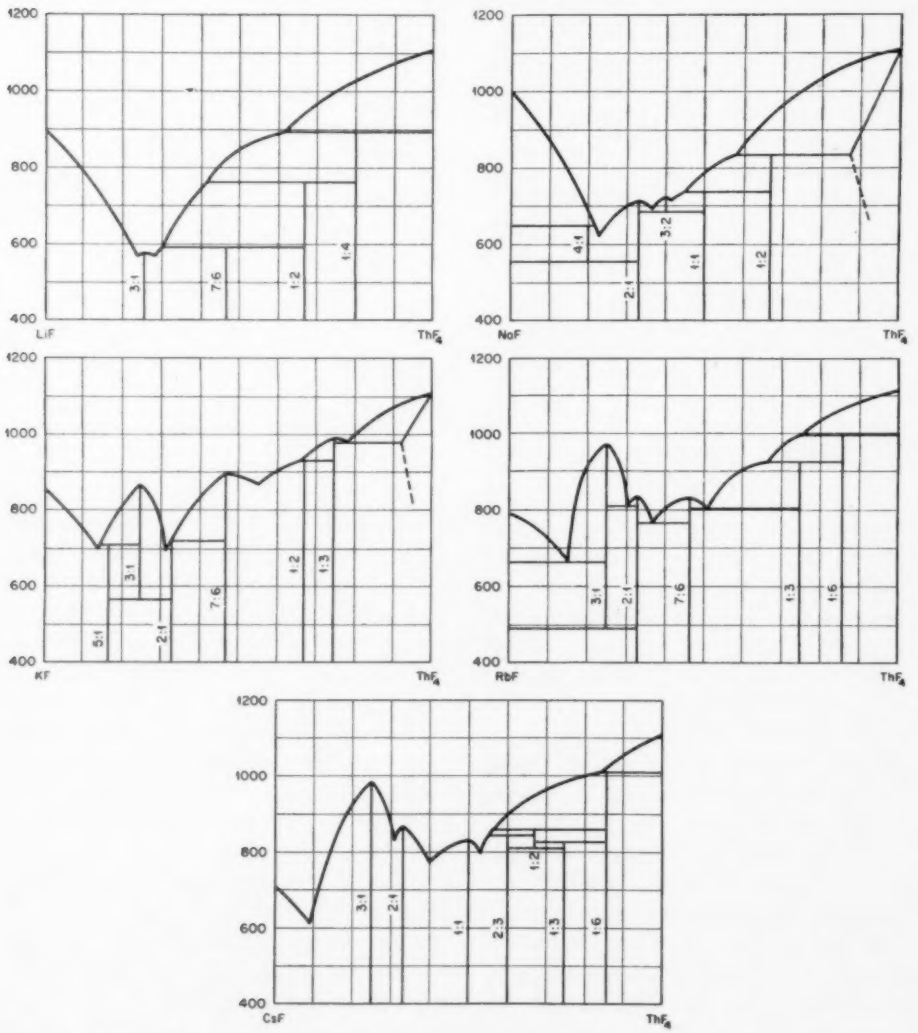

FIG. 2.—The binary systems of alkali fluorides and ThF_4 (composition in mole per cent; temperature in °C).

[16] Reactor Chemistry Division Annual Report, ORNL–2931 (1959).

In the two systems $NaF–ThF_4$ and $KF–ThF_4$, ThF_4 forms solid solutions with the adjacent compound richest in ThF_4, $NaF·2ThF_4$ and $KF·3ThF_4$, respectively. Except for these two solid solutions, no equilibrium solid solubility is reported among compounds in the binary systems.

It is remarkable that of a total of twenty-seven compounds reported in the various binary systems, only six of these are considered to exhibit polymorphic transitions.

In Fig. 2 are shown the phase equilibria of the five binary systems of alkali fluorides with ThF_4. The phase diagrams of the systems $KF–ThF_4$ and $RbF–ThF_4$, shown in Fig. 2, are recent modifications discussed elsewhere.[17]

Acknowledgements—It is a pleasure for Mr. CARLTON to acknowledge the invaluable advice and assistance provided by H. INSLEY and C. F. WEAVER concerning the use of the petrographic microscope, to T. N. MCVAY for similar assistance, and to H. A. FRIEDMAN for instruction and assistance with the experimental operations. We are also indebted to J. E. RICCI for helpful advice and suggestions concerning some aspects of the discussion of comparisons among systems. Special thanks are due to W. R. GRIMES for his encouragement and support of the work.

[17] R. E. THOMA, C. F. WEAVER and H. A. FRIEDMAN, To be published.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 98 to 101. Pergamon Press Ltd.

THE SYSTEM CdO–H_2O

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(*Received* 4 *April* 1960; *in revised form* 5 *July* 1960)

Abstract—The system CdO–H_2O has been studied at high temperatures and water pressures up to 3000 bars, and the *p–t* curve for the reaction $Cd(OH)_2 \rightleftharpoons CdO + H_2O$ is presented. The kinetics of the dehydration of $Cd(OH)_2$ in an essentially water-free atmosphere were also investigated. Values of $\Delta H_{react.}$ and the activation energy of dehydration have been calculated.

THE reaction $MO + H_2O \rightleftharpoons M(OH)_2$, where MO has the rock-salt and $M(OH)_2$ the brucite structure, can be studied for several different cations. Systematic study of such a series of analogous reactions might enable correlations to be made between the thermodynamic values obtained and the properties of the cations concerned, structural considerations having been eliminated.

Data for the equilibrium p–t curves for the ions Mg^{2+}, Ca^{2+}, Ni^{2+}, and Mn^{2+}[(1–5)] have previously been obtained in this laboratory. The present work deals with data for another cation, cadmium, which has not previously been studied.

EXPERIMENTAL

The starting materials for the study were as follows: [(1) $Cd(OH)_2$. From a solution of C.P. Cadmium Nitrate, $Cd(OH)_2$ was precipitated by addition of excess NaOH solution; the precipitate was filtered and washed on a Büchner funnel. Washing was continued until the filtrate showed no reaction to phenolphthalein. The precipitate was dried overnight at 100°C and ground in an agate mortar.

(2) CdO. $Cd(OH)_2$, prepared as described above, was heated to about 900°C, for a short time (because of the volatility of CdO). Decomposition was rapid, and the material produced was very reactive.

Powder X-ray diffraction patterns for both compounds agreed well with those in the ASTM X-ray powder data file and showed no trace of impurities (such as carbonate). The card for $Cd(OH)_2$, however, is not of high accuracy and shows a discrepancy between the values of a_0 and c_0 quoted, and those calculated from the powder data given. Accordingly, the powder pattern for $Cd(OH)_2$ was redetermined, using a Norelco high-angle diffractometer, with silicon as an internal standard. The new data are given in Table 1.

The hydrothermal studies were made using "test-tube" (or cold-seal) vessels at pressures up to about 3000 bars. The samples were contained in gold foil envelopes, and in every run but one both $Cd(OH)_2$ and CdO were used. Temperatures were automatically controlled, and measured using a chromel–alumel thermocouple and a Brown automatic precision indicator, and they are accurate to ±5°C. Pressures were measured on a Bourdon gauge, calibrated against a secondary standard, and are accurate to better than ±5 per cent.

For the kinetic studies, the sample was contained in a small open platinum boat, which was placed in a horizontal furnace. The temperature was controlled to ±3°C with a Honeywell controller, and

(1) D. M. ROY and R. ROY, *Amer. Mineral* **39**, 972 (1954).
(2) D. M. ROY and R. ROY, *Amer. Mineral* **39**, 957 (1954).
(3) D. M. ROY and R. ROY, *Amer. J. Sci.*, **225**, 574 (1957).
(4) C. KLINGSBERG and R. ROY, *Amer. Mineral* **44**, 819 (1959).
(5) P. J. WYLIE and O. F. TUTTLE, *J. Amer. Ceram. Soc.* **42**, 448 (1959).

measured with a chromel–alumel thermocouple placed immediately above the sample. The atmosphere in the furnace was controlled by passing a slow stream of nitrogen (purified in a train of soda-lime and silica-gel tubes) through the furnace tube under a slight positive pressure.

Runs were made at temperatures ranging from 86°C to 190°C. Weighings were made by removing the sample at suitable regular intervals, cooling rapidly on a brass block, and weighing on a semi-micro balance. The weighings were completed in less than a minute, and there appeared to be no trouble from CO_2 contamination.

TABLE 1.—X-RAY DIFFRACTION PATTERN FOR $Cd(OH)_2$

$d_{obs.}$ (Å)	I/I_0	hkl	$d_{calc.}$ (Å)
$4{\cdot}7_3$	70	00·1	4·70
$3{\cdot}02_8$	65	10·0	$3{\cdot}02_8$
$2{\cdot}54_7$	100	10·1	$2{\cdot}54_5$
$2{\cdot}34_4$	7	00·2	$2{\cdot}35_1$
1·857 ± 0·001	35	10·2	1·857
1·748	20	11·0	1·748
1·513	6	20·0	1·514
1·441	8	20·1	1·441
1·398	8*	10·3	1·392
		11·2	1·403
1·274	6	20·2	1·273
1·142	4	21·0	1·144

Unit cell

a = 3·496 Å c = 4·702 Å

* Doublet

RESULTS

The p–t curve for the equilibrium reaction is shown in Fig. 1. It was found that the CdO produced by rapid heating of $Cd(OH)_2$ readily reconverted to the hydroxide when held under appropriate p–t conditions, (and indeed showed a slight tendency to hydrate on quenching from the CdO field) so that no trouble was experienced in reaching equilibrium from this direction. On the other hand, it was found that at points just inside the CdO field, $Cd(OH)_2$ samples yielded CdO which had crystallized in extremely well-formed black octrahedra. This well crystallized "black" CdO would not rehydrate when held in the $Cd(OH)_2$ field, even after several days.

Well crystallized $Cd(OH)_2$ was also prepared from a run at 7 bars and 222°C. It crystallized in deep hexagonal "hoppers" characteristic of phases growing with spiral steps. It was found to be uniaxial negative, $n_\omega = 1{\cdot}802 \pm 0{\cdot}004$, $n_\varepsilon = 1{\cdot}70$. No evidence for the systematic formation of $Cd(OH)_2$ polytypes was found. In one isolated case a sample giving a completely inexplicable X-ray powder pattern was obtained; but this did not correspond to a recognizable polytype; all attempts to repeat the observation were unsuccessful.

The p–t curve was used to determine values for $\Delta H_{p,t}$ by means of the Clapeyron relationship; using the value of ΔH corresponding to 500 bars and 279°C, calculation by means of the integrated van't Hoff relation gave an equilibrium temperature of − 11°C at one bar. In the latter calculation corrections were applied throughout for the fugacity of water. Table 2 sets out some points in the curve together with corresponding values of ΔH.

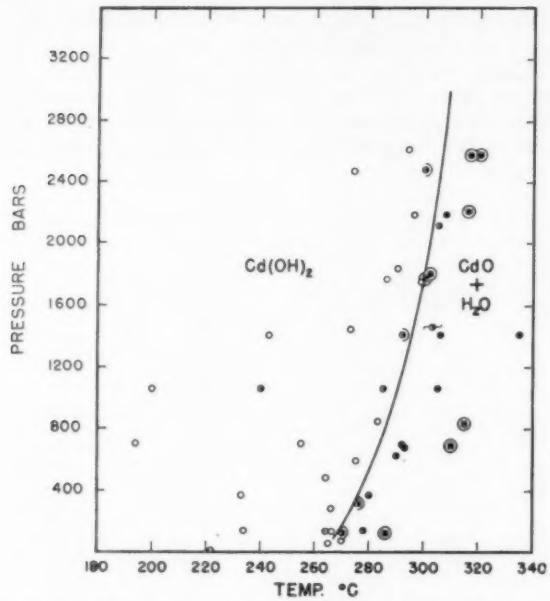

FIG. 1.—*P–t* equilibrium diagram for the system Cd–H_2O. Open circles: $Cd(OH)_2$. Filled circles: CdO. Double circles: well crystallized octahedra of CdO.

TABLE 2.—ΔH_r FOR THE REACTION $Cd(OH)_2 \rightleftharpoons CdO + H_2O$*

Pressure (bars)	Temp. (°C)	ΔH (kcal)
2000	303	7·5
1000	289	4·7
500	279	4·2

* These values are not particularly accurate as they necessarily were read from slopes of smooth lines drawn as the best fit to experimental points.

For the kinetic studies, curves were plotted of per cent material dehydrated against time and the rate used in calculations was the initial rate. This varied from about 1×10^{-3} per cent per hour at 86° to 11 per cent per hour at 190°. By plotting in the usual way, a value of 28·8 kcal is obtained for the activation energy of this reaction. This relatively high value partly explains why $Cd(OH)_2$ does not decompose spontaneously under ambient conditions, as would be implied from the *p–t* results.

DISCUSSION

As shown in Table 3 the equilibrium temperature at 1000 bars is much higher for Mg and Ca (extrapolated) than for Ni, Mn and Cd. This difference must therefore be related to the increase in covalency of the bond rather than to ionic size. Considering now the pairs Ca–Mg and Mn–Ni, the temperature decreases with ionic size for elements of approximately the same degree of polarizability. Cadmium, larger than either Mn or Ni shows a lower temperature than either. One must conclude that

TABLE 3.—COMPARISON OF EQUILIBRIUM DEHYDRATION TEMPERATURES AT 1000 BARS

Cation	Goldschmidt radius	Equil. temp. (°C) at 1000 bars	ΔH (kcals)
Mg	0·78	650	8·84–9·79
Ni	0·78	300	
Mn	0·91	380	
Cd	1·03	290	4–7
Ca	1·06	>1000*	(26·5)

* This value extrapolated by calculation: $Ca(OH)_2$ melts below this temperature (see Ref. 5).

this is because the Cd—O bond is considerably more covalent than the Ni—O and Mn—O bonds; this seems not to be unreasonable.

Values for $\Delta H_{react.}$ are not well enough known for any correlations with ionic properties to be established at the present time.

Acknowledgement—Financial support for the experimental work was provided by the National Science Foundation (Grant G4648).

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J. Inorg. Nucl. Chem. 1961, Vol. 17, pp. 102 to 107. Pergamon Press Ltd.

NIOBDIHYDRID, NbH_2

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(*Received* 6 *August* 1960)

Abstract—Niobium dihydride was prepared in a pure form by cathodic hydrogenation of niobium metal. Its homogeneity range extends from $NbH_{2\cdot00}$ to ca. $NbH_{2\cdot07}$. It crystallizes with the fluorite structure and has a lattice constant of 4·563 Å. Niobium dihydride is unstable and decomposes into β-NbH and hydrogen.

IM System Niob–Wasserstoff treten nach BRAUER und HERMANN[1] bei Zimmertemperatur zwei Phasen auf, die α-Phase, die sich von Nb bis $NbH_{0\cdot11}$ erstreckt, und die β-Phase, deren Homogenitätsbereich von $NbH_{0\cdot70}$ bis $NbH_{0\cdot94}$ reicht und die vereinfacht als Niobmonohydrid bezeichnet wird. Die α-Phase kristallisiert kubisch raumzentriert mit einer Gitterkonstanten von 3·30–3·31 Å, die β-Phase kristallisiert in einer orthorhombischen Struktur, die durch geringfügige Verzerrung einer raumzentriert kubischen Zelle mit einer Gitterkonstanten von 3·41–3·46 Å entstanden gedacht werden kann. Diese Ergebnisse wurden inzwischen von anderen Autoren[2–5] in ihren Grundzügen bestätigt. Das im folgenden beschriebene Niobdihydrid NbH_2 erweitert als γ-Phase das System Niob-Wasserstoff zur wasserstoffreichen Seite hin.

Darstellung von Niobdihydrid

Wir beobachteten die Entstehung von Niobdihydrid zuerst bei der Einwirkung von verdünnter Flusssäure auf Niobmetallpulver. Dabei laufen die Reaktionen ab:

$$Nb + 5HF + nF^- \rightarrow NbF_{5+n}^{n-} + 5H \quad (1)$$

$$Nb + H \rightarrow NbH \quad (2)$$

$$NbH + H \rightarrow NbH_2 \quad (3)$$

Da die beiden Hydride sich in Flusssäure mit ähnlicher Geschwindigkeit lösen wie das Niobmetall, besteht das Reaktionsprodukt stets aus einem Gemenge aller drei Stoffe, aus dem erst gegen Ende der Reaktion das Metall langsam verschwindet, jedoch nicht das Niobmonohydrid. Frei von röntgenographisch erkennbaren Verunreinigungen konnten wir das Niobdihydrid jedoch herstellen, wenn wir von feinteiligem Niobmonohydrid ausgingen und dieses mit Flusssäure behandelten. Nach mehrstündiger Einwirkung der Flusssäure war das entstandene Niobdihydrid frei vom Ausgangsstoff. Niobmetall und die beiden Hydride geben charakteristische Debye-Scherrer-Diagramme und sind deshalb in den Reaktionsprodukten leicht zu identifizieren. Über

[1] G. BRAUER und R. HERMANN, *Z. anorg. Chem.* **274**, 11 (1953).
[2] W. TRZEBIATOWSKI und B. STALINSKI, *Bull. Acad. Pol. Sc.*, Cl. III, **1**, 131 (1953).
[3] C. WAINWRIGHT, *J. Inst. Metals.* **4**, 68 (1957/58).
[4] W. M. ALBRECHT, M. W. MALLET und W. D. GOODE, *J. Elektrochem. Soc.* **105**, 219 (1958).
[5] W. M. ALBRECHT, W. D. GOODE und M. W. MALLETT, *J. Electrochem. Soc.* **106**, 981 (1959).

die Auffindung des Niobdihydrids haben wir bereits in kurzen Mitteilungen berichtet.[6,7]

Die Flusssäureätzung von Niobmonohydrid lieferte allerdings kein reines Niobdihydrid. Aus dem Verhältnis von Einwaage und Wasserstoffgehalt ergab sich günstigstenfalls ein Verhältnis von H:Nb = 1·60:1. Der Wasserstoffgehalt sank mit der Dauer der Flusssäurebehandlung. Auch der Niobgehalt der Präparate lag unter dem für NbH_2 zu erwartenden Wert von 97·88% und betrug im besten Falle ca. 95%; auch er sank mit der Ätzdauer. Der Rest bestand im wesentlichen aus Sauerstoff: Die röntgenographische Analyse des Rückstandes der Wasserstoffanalyse (vgl. S. 106) ergab, dass darin ausser dem erwarteten Niobmetall erhebliche Mengen Niobmonoxyd, NbO, enthalten waren. Der Sauerstoff gelangt wahrscheinlich durch Hydrolyse der Fluorniobate, wie sie bei der Flusssäurebehandlung entstehen, in den Rückstand und liegt zunächst in Form von röntgenamorphem Niobpentoxyd vor. Bei der hohen Temperatur der Wasserstoffanalyse wird Niobpentoxyd dann durch das Metall zu Niobmonoxyd reduziert. Berechnet man den Sauerstoffgehalt aus der Differenz des Niob- und Wasserstoffgehaltes gegen 100% und korrigiert dann den Niobgehalt um die zur Bindung von 5 O als Nb_2O_5 erforderlichen 2 Nb, so erhält man ein Verhältnis von H:Nb = 1·90 bis 1·95. Dieses Verhältnis verschiebt sich noch weiter in Richtung auf das zu erwartende von 2·00:1, wenn man berücksichtigt, dass ein gewisser Anteil an Nichtmetallatomen (O, N, C) wegen der ursprünglichen Verunreinigung der Ausgangssubstanz in Form einer festen Lösung vorlag und wahrscheinlich mehr als die den Formeln Nb_2O_5, Nb_2N oder Nb_2C entsprechende Zahl von Niobatomen an einer Hydridbildung hinderte.

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Entsprechend den Reaktionsgleichungen (2) und (3) sollte sich Niobdihydrid aus Niobmetall und atomarem Wasserstoff darstellen lassen. VUKANOVIC und Mitarbeiter[8] haben dies untersucht, jedoch blieb die Wasserstoffaufnahme so gering, dass noch nicht einmal die Bildung der β-Phase beobachtet wurde. Die Ursache dürfte darin zu suchen sein, dass die Reaktion nur äusserst langsam verläuft. Dafür sprechen auch die Beobachtungen bei der Einwirkung von atomarem Wasserstoff auf Tantal.[9]

Wir fanden nun in der kathodischen Hydrierung von an Golddrähten befestigten Niobmetallblechen eine geeignete Methode zur Darstellung des Niobdihydrids. Der Vorteil dieses Verfahrens liegt vor allem auch darin begründet, dass weder Niob noch Niobmonohydrid von der als Elektrolyt benutzten verdünnten Schwefelsäure im mindesten angegriffen werden; im Laufe der Arbeit stellte sich heraus, dass dies auch für das Niobdihydrid gilt. Besondere Bedeutung hat hingegen die richtige Wahl des Anodenmaterials. Platin und Platinlegierungen erwiesen sich hierbei als völlig ungeeignet. Bei unseren Elektrolysebedingungen trat eine geringfügige Korrosion der Pt-Anoden ein, die von sekundärer Abscheidung des aufgelösten Platins am Niob und auch am Golddraht begleitet war. Die geringen Mengen des feinverteilt wieder abgeschiedenen Platins führten nun offensichtlich zu einem Zusammenbruch der Überspannung des Wasserstoffs am Niob. Als Reaktionsprodukt wurde in diesen Fällen vorwiegend Niobmonohydrid erhalten, die weitere Hydrierung zu Niobdihydrid verlief in unreproduzierbarer Weise entweder nur in geringem Ausmass oder unterblieb ganz. Verwendet wurden schliesslich als Anoden Stäbe aus Borcarbid. Zwar wurden sie unter Bildung von Borsäure und wahrscheinlich Kohlensäure und unter Abscheidung eines feinteiligen schwarzen Schlammes korrodiert, doch hatte dies keinen nachteiligen Einfluss auf die gewünschte Hydrierung des Niobs.

[6] G. BRAUER und H. MÜLLER, *Angew. Chem.* **70**, 53 (1958).
[7] G. BRAUER und H. MÜLLER, *Hochschmelzende Metalle*, 3. Plansee-Seminar, 257 (1958).
[8] V. M. VUKANOVIC, V. M. MILUTINOVIC und S. S. MALCIC, *C.R. Acad. Sci., Paris* **241**, 1298 (1955).
[9] E. PIETSCH und H. LEHL, *Kolloidz.* **68**, 226 (1934).

Die Niobbleche wurden vor der Hydrierung im Hochvakuum bei 2000°C ausgeglüht. Dies geschah aus zwei Gründen. Erstens wurde durch diese Behandlung die vom Walzvorgang her vorhandene dünne Oxydschicht weitgehend entfernt. Das führte zu einer starken Herabsetzung der Induktionsperiode am Beginn der Elektrolyse, während welcher die Wasserstoffentwicklung nur am Golddraht stattfindet. Man wird sich dazu vorstellen müssen, dass eine Hydrierung erst nach Reduktion der oxydischen Oberflächenschicht einsetzt. Zweitens zerfallen ungetemperte Bleche während der Hydrierung, und die herabfallenden Stücke sind oft noch nicht vollständig in das Dihydrid umgewandelt. Angelassene und somit rekristallisierte Bleche hingegen werden unter sichtlicher Volumenvermehrung nur von mehr oder minder starken Rissen durchzogen. Die vollständige Hydrierung erforderte bei unseren Bedingungen zwei bis vier Tage und verläuft in zwei Stufen. Während des ersten Schrittes, der etwa ein Zehntel der Gesamtzeit benötigt, läuft vorzugsweise die Reaktion (2) ab, während des zweiten die Reaktion (3). Ein Gleichgewichtszustand liegt während der Hydrierung nicht vor, bald nach Beginn der Elektrolyse finden sich alle drei möglichen Phasen Niob, Niobmonohydrid und Niobdihydrid nebeneinander, wie dies im Prinzip auch bei anderen heterogenen Reaktionen beobachtet wird.

Die einzige Verunreinigung des Endproduktes war Niobmonohydrid in jenen Fällen, in denen die Hydrierung zum Dihydrid noch nicht vollständig verlaufen war. Solche Präparate besassen höchstens einen Wasserstoffgehalt entsprechend $NbH_{1\cdot99}$. Daraus folgt, dass sich zwischen $NbH_{0\cdot94}$ und $NbH_{1\cdot99}$ ein Zweiphasengebiet erstreckt. Von der Zusammensetzung $NbH_{2\cdot00}$ ab ist das Dihydrid frei von Niobmonohydrid, wie sich aus der für Gemenge von Niobmonohydrid und Niobdihydrid sehr empfindlichen röntgenographischen Analyse ergibt. Niobdihydrid vermag jedoch noch weiteren Wasserstoff aufzunehmen, ohne dass erneut eine Phasenumwandlung eintritt. Als Verbindung maximalen Wasserstoffgehaltes wurde $NbH_{2\cdot07}$ erhalten. Diese Zusammensetzung ist jedoch nicht in irgendeiner Weise bevorzugt, sondern nur zufällig experimentell bedingt. Dass Wasserstoff vom Niobdihydrid auch noch über $NbH_{2\cdot07}$ hinaus aufgenommen werden kann, ist nämlich sehr deutlich bei Beendigung der Elektrolyse zu sehen. Die Wasserstoffentwicklung am Niobdihydridblechstück hört dann nicht sofort auf. Über einen Zeitraum von 10 bis 15 Minuten hinweg perlt weiterhin Wasserstoff auf. Seine Menge wurde nicht bestimmt, sie war jedoch gering und dürfte den Gesamtwasserstoffgehalt des Hydrids allenfalls bis zu einem Wert von $NbH_{2\cdot10}$ erhöhen. Dieser Wasserstoff ist durch die Elektrolyse in das Dihydridgitter hineingepresst worden und wird nach ihrem Ende sofort wieder abgegeben. Beim Palladiumhydrid ist dieser Effekt seit langem bekannt.[10]

Kristallstruktur von Niobdihydrid

Niobdihydrid kristallisiert mit einer kubisch flächenzentrierten Anordnung der Niobatome. Die Gitterkonstante beträgt $4\cdot563 \pm 0\cdot001$ Å. Die Gitterkonstante bleibt innerhalb des angegebenen Fehlerbereiches konstant über den Homogenitätsbereich der Verbindung. Die gemessene Dichte von $6\cdot6 \pm 0\cdot2$ g cm^{-3} steht mit der Röntgendichte von $6\cdot63$ g cm^{-3} in Einklang. Die Lage der Wasserstoffatome ist röntgenographisch nicht bestimmbar. In Analogie zu Dihydriden anderer

[10] D. P. SMITH, *Hydrogen in Metals*. Univ. of Chicago Press (1948).

Übergangsmetalle[11–16] nehmen wir an, dass der Wasserstoff sich in den Tetraederlücken befindet und Niobdihydrid damit Flussspatstruktur hat. Über die Formel $NbH_{2\cdot00}$ hinaus vorhandener Wasserstoff wird in den Oktaederlücken lokalisiert sein.

Eigenschaften von Niobdihydrid

Niobdihydrid ist eine recht instabile Verbindung. Bringt man sie sofort nach ihrer Herstellung in ein Vakuum von etwa 10^{-6} Torr, so gelingt es, etwa die Hälfte des Wasserstoffs in kurzer Zeit abzupumpen, wobei reines Niobmonohydrid zurückbleibt. Beträgt das Vakuum nur 10^{-3} Torr, so erfolgt der Zerfall erheblich langsamer, nach 30 Minuten ist erst etwa 5% zerfallen. Eine Überwachung des Vakuums zeigt, dass der Zerfall nicht sofort, sondern erst nach einigen Minuten einsetzt. Hat der Zerfall jedoch erst einmal eingesetzt, so schreitet er auch nach Abtrennung der Pumpe noch weiter fort, wobei Drucke bis zu etwa 1 Torr erhalten wurden. Auch beim Aufbewahren an der Luft verliert Niobdihydrid Wasserstoff, und zwar zuerst den über die Formel $NbH_{2\cdot00}$ hinaus vorhandenen, dann tritt Umwandlung in Monohydrid ein. Der Wasserstoffverlust verläuft bei fein gepulverten Proben schneller als bei in kleinen Blechflittern vorliegenden. Bei ersteren treten nach etwa ein bis drei Tagen die ersten Niobmonohydrid-Röntgenlinien auf. Der weitere Zerfall ist dann allerdings recht langsam, so dass nach einem Monat erst etwa 10% der Verbindung zerfallen ist, mit von Probe zu Probe verschiedenem Zerfallsgrad. Dabei handelt es sich jedoch nicht um eine einfache Wasserstoffabgabe; es scheint auch eine geringe Oxydation mitzuspielen, da gepulverte Präparate in den ersten drei Tagen dieser Lagerung um etwa 0·2% an Gewicht zunehmen. Solches gealterte unreine Niobdihydrid gibt seinen Wasserstoff auch bei mehrstündigem Aufbewahren in einem Vakuum von 10^{-6} Torr nicht schneller ab. Der Wasserstoffverlust friert nach einiger Zeit ein. Manche unserer Präparate enthielten noch nach einem Jahr ca. 75% Niobdihydrid.

Zur Erklärung dieser Eigenschaften nehmen wir an, dass die Verbindung sich nach Ende der Elektrolyse mit einer Oxydhaut überzieht, welche die Rekombination von an die Oberfläche diffundierenden Wasserstoffatomen behindert und damit den zu erwartenden Zerfallsprozess überhaupt. Diese Oberflächenoxydation steht in Übereinstimmung mit der beobachteten Gewichtszunahme bei der Lagerung. Ein Zerfall des Niobdihydrids kann dann nur dadurch fortschreiten, dass der molekulare Wasserstoff aus Defekten der Oxydschicht entweicht. Dies erklärt die starke Abhängigkeit von der Güte des angelegten Vakuums: Nur sehr hohes Vakuum vermag den durch Kapillarkräfte in den Rissen der Oberfläche blockierten Wasserstoff schnell zu entfernen und damit eine weitere Wasserstoffabgabe zu ermöglichen. Unter mechanischer Erweiterung des Risses kann dann die Wasserstoffabgabe auch bei höheren Drucken fortschreiten, solange sich keine neue Oxydschicht bildet.

Die Instabilität des Niobdihydrids ist nicht unerwartet. Bei der Bildung aus Niob und atomarem Wasserstoff braucht das System keine Dissoziationsenergie zur Wasserstoffmolekülspaltung zu leisten; diese Energie steht gegenüber einer H_2-Hydrierung

[11] T. R. P. Gibb Jr. und H. W. Kruschwitz Jr., *J. Amer. Chem. Soc.* **72**, 5365 (1950).
[12] R. E. Rundle, C. G. Shull und E. O. Wollan, *Acta Cryst.* **5**, 22 (1952).
[13] S. S. Sidhu, *Acta Cryst.* **7**, 447 (1954).
[14] R. N. R. Mulford und G. E. Sturdy, *J. Amer. Chem. Soc.* **77**, 3449 (1955).
[15] C. E. Holley Jr., R. N. R. Mulford, F. H. Ellinger, W. C. Koehler und W. M. Zachariasen, *J. Phys. Chem.* **59**, 1226 (1955).
[16] G. E. Sturdy und R. N. R. Mulford, *J. Amer. Chem. Soc.* **78**, 1083 (1956).

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zusätzlich zur Verfügung und ermöglicht die Bildung eines höheren Hydrides. Nach Beendigung der Elektrolyse, d.h. nach Rückkehr zu Normalbedingungen, wird der Wasserstoffüberschuss dann wieder abgegeben.

Mit Niobdihydrid ist zum ersten Mal ein metallisches Hydrid dargestellt worden, das durch normale Hydrierung mit Wasserstoff nicht erhältlich ist. Seiner Verwendung als Moderator zur Abbremsung von Neutronen in Kernreaktoren steht die grosse Instabilität im Wege, die jedoch vielleicht durch Zulegieren anderer Metalle verbessert werden könnte.

Darstellung von Niobdihydrid durch Flusssäurebehandlung

Als Ausgangsmaterial diente Niobmonohydrid der Metal Hydrides Inc., Beverley, Mass., USA, von 10000 mesh. Aus dem Niob- und Wasserstoffgehalt errechnete sich eine Formel $NbH_{0.86}$, an Fremdstoffen enthielt das Produkt ca. 0·7% Kohlenstoff, Stickstoff und Sauerstoff und geringe Spuren von Metallen. Bei einem einzelnen Versuch liessen wir etwa 2 g des Materials in einer Platinschale mit 40 ml ca. 10-proz. Flusssäure unter gelegentlichem Umrühren vier Stunden lang stehen. Dann wurde vorsichtig abdekantiert, der Rückstand mehrmals mit Aceton gewaschen und schliesslich bei 60°C getrocknet. Auf Abwesenheit von Niobmonohydrid wurde röntgenographisch geprüft, Verunreinigungen der Ausgangssubstanz (Nb_2N) fanden sich auch im Endprodukt wieder.

Darstellung von Niobdihydrid durch elektrolytische Hydrierung

Niobbleche von 1 cm^2 Grösse und 0·1 mm Dicke wurden ca. 15 Minuten in einem Hochfrequenzinduktionsofen bei 2×10^{-4} Torr auf 2000°C erhitzt. Reste von Nichtmetallen werden bei dieser Behandlung ausgetrieben, der Niobgehalt betrug bei unseren Proben 99·9%. Die Niobbleche wurden mit einem Golddraht von 0·3 mm Stärke umwickelt und als Kathode geschaltet. Man musste dabei auf guten Kontakt zwischen Gold und Niob achten. Als Anoden dienten Borcarbidstäbe von 6 × 12 mm Querschnitt und 70 mm Länge des Elektroschmelzwerkes Kempten GmbH. Sie wurden am einen Ende mit einer dünnen Aluminiumfolie umwickelt und fest zwischen zwei Messingstäben eingespannt. Zum Schutz gegen Säurespritzer wurden der obere Teil der Borcarbidstäbe und die Messinghalterung mit Araldit (Ciba) bestrichen. Als Elektrolyt wurde 6 n Schwefelsäure verwendet, die gelegentlich zur Vermeidung von Borsäureausscheidungen ausgewechselt wurde. Die Anoden sollen nicht tiefer als 8 mm eintauchen. Als Abstand zwischen beiden Elektroden wurde ca. 3 cm gewählt, die Elektrolyse erforderte bei 3 V und 100 mA zwei bis vier Tage bis zur restlosen Umwandlung des Metalls in das Dihydrid. Nach Beendigung der Elektrolyse wurde das Blech mitsamt der Goldhalterung mit Aceton abgespült und an der Luft getrocknet.

Analyse der Hydride

Zur Bestimmung des Niobgehaltes wurde eine Probe bei 850°C verbrannt und der Niobgehalt aus dem ausgewogenen Niobpentoxyd berechnet.

Zur Wasserstoffanalyse diente eine Vakuumapparatur, bestehend aus Quecksilberdiffusionspumpe, McLeod-Manometer, Ofen und Töplerpumpe (automatisches Modell der Fa. Ströhlein, Düsseldorf). Wir brachten die Analysenprobe von ca. 30 mg in den kalten Ofen und evakuierten dann die Anlage. Vor allem bei frisch hergestellten Proben durfte diese Vorevakuierung nur wenige Minuten andauern, da danach schon der Zerfall des Niobdihydrids begann, wie am Ansteigen des Druckes festzustellen war. Auf keinen Fall durften Quecksilberdämpfe zwischen Pumpe und Ofen durch eine Kühlfalle ausgefroren werden, da die dadurch hervorgerufene Verbesserung des Vakuums den Niobdihydridzerfall erheblich beschleunigte. Bei mehrere Tage alten Präparaten sind diese Vorsichtsmassnahmen unnötig, natürlich auch bei den durch Flusssäureätzung hergestellten. Nach Abtrennung der Pumpe wurde der Ofen innerhalb einer Stunde auf 1000°C aufgeheizt. Der Dihydridzerfall verlief in zwei Stufen entsprechend den Umkehrungen der Reaktionsgleichungen (3) und (2). Die Temperaturen, bei denen die Wasserstoffabgabe erfolgte, waren abhängig von der Erhitzungscharakteristik; wir beobachteten die Wasserstoffabgabe bei etwa 250 und dann wieder bei etwa 400°C. Der entwickelte Wasserstoff wurde vollständig abgepumpt und nach Berücksichtigung einer geringen Totleistung der Pumpe auf Normalbedingungen umgerechnet. Eine Analyse mittels eines Mikrogasanalysators nach

Feichtinger (Fa. Ströhlein, Düsseldorf) erwies das abgepumpte Gas innerhalb der Fehlergrenzen als reinen Wasserstoff. Das nach der Dehydrierung zurückgewogene Niob und der Wasserstoff summierten sich bei den besten Analysen zu 99·9%, wie dies bei Verwendung von Niobmetall von 99·9% zu erwarten ist. Niedrigere Summenwerte (schlechtestenfalls 99·6%) führen wir darauf zurück, dass bei der Dehydrierung eine geringe Menge des Materials aus dem Schiffchen herausstäubt und sich so der Rückwägung entzieht.

Wir danken den Herren Dr. G. L. MILLER, Murex Ltd., Rainham, Essex und Dr. R. LESSER, Heraeus GmbH., Hanau, für Überlassung von geeignetem Niobblech. Die Herren Dr. KAISER und Dr. ADLASSNIG, Elektroschmelzwerke Kempten GmbH., Kempten (Allgäu) haben unsere Arbeiten durch kostenlose Überlassung der Borcarbidstäbe wesentlich unterstützt. Der Verdand der Chemischen Industrie und die Deutsche Forschungsgemeinschaft förderten die Arbeit in dankenswerter Weise durch Sachmittel. Das Gerät zur Gasanalyse wurde vom Bundeswirtschaftsministerium zur Verfügung gestellt.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 108 to 111. Pergamon Press Ltd.

ON THE BORON–SILICON REACTION

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(*Received* 28 *June* 1960; *in revised form* 4 *August* 1960)

Abstract—In contrast to previously reported attempts to prepare boron silicide, it is demonstrated that amorphous boron and crystalline silicon react in a solid state reaction in air or in inert atmosphere to form two compounds. Below 1370°, B_4Si is the phase observed. Above 1370°, B_6Si results. B_4Si undergoes disproportionation into B_6Si above about 1100°. Some solid solution of boron and/or boron silicide in silicon occurs during the synthesis of boron silicide.

THE first reported compounds of boron and silicon were described by MOISSAN and STOCK[1] in 1900. They passed an electric current through a mixture of the elements and obtained a mixture of boron silicides,* B_6Si and supposedly B_3Si. Subsequently, other workers became interested in this system and also attempted to prepare combinations of boron and silicon. WATTS[2] could not make any definite compositions by reacting boron with silicon at high temperatures. TONE[3] attempted to remove carbon from silicon carbide–boron carbide mixtures, but failed to obtain any evidence for boron–silicon compounds. Over a decade elapsed between TONE's work and the next reported observation on boron silicide. In 1951, BREWER and co-workers[4] made a study of some refractory borides. Two silicon samples with 50 and 80 atomic per cent of boron were heated in beryllia crucibles for 20 min at 1725°. No evidence for any boron–silicon combination was found, only X-ray lines for silicon being observed. Five years later, in 1956, STAVROLAKIS and co-workers[5] made a study of some boride cermets. During the course of this work, they reacted mixtures of boron and silicon at 1400° and also concluded that no boron silicides result at this temperature. In 1958, CLINE[6] reported some preliminary crystallographic data on B_6Si and later[7] gave more physical data on single crystals of the compound obtained by fusing the elements at 2250° in argon atmosphere. ADAMSKY[8] completely characterized B_6Si, using CLINE's single crystals.

Besides B_6Si, the only other substantiated phase in the boron–silicon system is the newly reported B_4Si.[9,10]

* The writer suggests the nomenclature "boron silicide" in contrast to "silicon boride" in consistency with the boron-carbon system in which B_4C is called "boron carbide".

[1] H. MOISSAN and A. STOCK, *C. R. Acad. Sci., Paris* **131**, 139 (1900).
[2] O. P. WATTS. Thesis, University of Wisconsin (1906). See also J. W. MELLOR, *A Comprehensive Treatise on Theoretical and Inorganic Chemistry*, V. 27. Longmans, Green, London (1946).
[3] F. J. TONE, *Industr. Engng. Chem.* **30**, 232 (1930).
[4] L. BREWER, D. L. SAWYER, D. H. TEMPLETON and C. H. DAUBEN, *J. Amer. Cer. Soc.* **34**, 173 (1951).
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[6] C. F. CLINE, *Nature, Lond.* **181**, 476 (1958).
[7] C. F. CLINE, *J. Electrochem. Soc.* **106**, 322 (1959).
[8] R. F. ADAMSKY, *Acta Cryst.* **11**, 744 (1958).
[9] C. F. CLINE and D. E. SANDS, *Nature, Lond.* **185**, 456 (1960).
[10] E. COLTON, *J. Amer. Chem. Soc.* **82**, 1002 (1960).

Two other boron–silicon phases in addition to B_6Si and B_4Si are referred to in the literature, complete substantiation not yet being available. These phases are B_3Si (originally reported by MOISSON) and a boron–rich composition $B_{10-12}Si$. SAMSONOV and LATYSHEVA in 1955[11] reported that B_3Si results from hot pressing the elements at 1600–1800° or from thermite reduction with magnesium of quartz and boric oxide. However, GUREVICH and co-workers[12] have questioned the results of SAMSONOV as well as the existence of B_3Si. In regards to the boron–rich boron silicide phase, little convincing evidence has been presented. A hard coating designated as SiB_x is reported to be vapour deposited at 1000–1300° from the reaction of silicon tetrachloride and boron trichloride.[13] Some evidence[14,15] points to the existence of $B_{12}Si$, possibly identical in structure with AlB_{12}. More definite work is needed to establish conclusively this high–boron phase.

EXPERIMENTAL STUDIES

Amorphous boron powder (about 80 per cent of which was −325 mesh) of 83–95 per cent purity was used, the major impurity being magnesium in some unknown form.[16] Some studies were made with crystalline boron of 99 per cent purity. The reaction rates were very slow compared with the amorphous material, and work with crystalline boron was not pursued. It was found that the impurities present in the boron tended to concentrate in the upper, slag-like layer of the reaction product; hence, pure boron silicide could be prepared as easily from 85 per cent boron as from 95 per cent boron. Each grade gave the identical product. Crystalline silicon (size distribution −100 mesh X down) of 98 per cent purity was used, the major impurities being iron and calcium. Crucibles of fire clay* were found to be satisfactory for these reactions. Some small amount of reaction at the interface was evident. Heating was by resistance in silicon carbide-heated furnaces. Loose, intimate mixtures of the elements or cold pressed specimens were used, and results are shown in Table 1. In two cases only were purifications carried out in order to identify conclusively the actual boron silicide produced. X-ray powder diffraction patterns were used to identify the products, the pattern for B_6Si[7] and for B_4Si[10,17] having been established earlier.

RESULTS

In attempts to prepare boron silicide, previous investigators heated the elements at temperatures considerably above 1400° (only STAVROLAKIS[5] used 1400°). Such high temperatures were undoubtedly used because boron melts at about 2300°, and it was probably assumed that fusion conditions would be necessary in order to effect reaction between boron and silicon.

We have found in this work as well as in a previous study[10] that boron and silicon react without fusion in a solid state reaction. Two temperatures seem to be critical in forming the two boron silicide phases definitely established: above about 1200° and below 1370°, B_4Si forms. Above 1370°, B_6Si only results.

* Denver Fire Clay Company, Denver, Colorado.

[11] G. V. SAMSONOV and V. P. LATYSHEVA, *Doklady Akad. Nauk SSSR* **105**, 499 (1955); *Chem. Abstr.* **50**, 7639h (1956).

[12] M. A. GUREVICH, V. A. EPEL'BAUM, and B. F. ORMONT, *Zh. Neorg. Khim.* **2**, 206 (1957). *Chem. Abstr.* **51**, 16181b (1957).

[13] C. F. POWELL, *High Temperature Technology* pp. 135, 145. (Edited by I. E. CAMPBELL), J. Wiley, New York (1956).

[14] H. NOWOTNY, R. KIEFFER and F. BENESOVSKY, *Planseeberichte* **5** (3), 86 (1957).

[15] H. NOWOTNY, E. PIEGGER, R. KIEFFER and F. BENESOVSKY, *Monatsh. Chem.* **89**, 611 (1958).

[16] J. BRATT, F. W. BERK and Company, Inc., Wood-Ridge, N. J. Private communication.
"... concerning the analysis of amorphous boron, it is known that boron forms a six-membered ring, which sequesters divalent atoms; in fact, it is believed that the magnesium is present in this form, rather than as MgO. The absence of an X-ray diffraction pattern for MgO, Mg_3B_2, MgB_4O_4, or other known magnesium compounds lends credence to this theory."

[17] V. I. MATKOVICH, *Acta Cryst.* **13**, 679 (1960).

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B_4Si appears to be unstable above about 1370°. Bodies of B_4Si when heated in air or inert atmosphere for only two hours at 1370° showed no B_4Si on X-ray examination of the resulting piece. Only B_6Si and silicon were observed. The disproportionation

$$3B_4Si = 2B_6Si + Si$$

occurs and is rapid at 1370° although occurring at a slower rate below 1370°. This disproportionation in boron silicide is not without precedent, for recently WATTERS and DEWITT[18], in a study of the phosphides and arsenides of boron, have reported

TABLE 1.—REACTION OF BORON AND SILICON

Example	Molar ratio boron:silicon	Temperature (°C) of reaction (°C)	Soak at reaction temperature (hr)	Atmospheres	X-Ray analysis of reaction products*		
					Si	B_6Si	B_4Si
1	2:1	1210	12	A	*s*	—	*vw*
2	2:1	1260	12	A	*s*	—	*vw*
3	2:1	1370	2-3	A	*w*	*tr*	*s*†
4	4:1	1370	2	Stagnant air‡	*w*	*w*	*ms*
5	4:1	1370	48	Stagnant air‡	*m*	*mw*	—
6	2:1	1430	2	A	*ms*	*w*	—
7	1:1	1430	4	He	*vs*	*vw*	—
8	2:1	1430	4	He	*ms*	*w*	—
9	3:1	1430	4	He	*m*	*m*	—
10	4:1	1430	4	He	*w*	*s*	—
11	6:1	1430	4	He	—	*vs*†	—
12	10:1	1430	14	He	*tr*	*vw*	—
13	10:1	1710	6	H_2	*vs*	*vw*	—

* X-ray designations: *vs*, very strong; *ms*, medium strong; *s*, strong; *m*, medium; *mw*, medium weak; *w*, weak; *vw*, very weak; *tr*, trace (barely detectable).

† Typical chemical analysis on purified products.

B_4Si: B, 60·6%; Si, 36·8%; Mg, 0·7%; B/Si = 4·28

B_6Si: B, 69·7%; Si, 29·5%; Mg, 1·3%; B/Si = 6·14

‡ This reaction product also contained some boron nitride.

the analogous disproportionations in which BP loses phosphorus to form B_6P (tentatively established) and BAs loses arsenic to form $B_{6-7}As$ (tentatively established).

We have been able to demonstrate conclusively that B_4Si results from heating boron and silicon as low as 1210° (example 1, Table 1). As the temperature is increased to 1370° and the reaction time decreased from 12 to 2 hr, B_4Si still forms and in increased amounts; but the presence of B_6Si is now also detected. We have not yet succeeded in preparing B_4Si completely free of B_6Si. The best preparation of B_4Si (example 3, Table 1) gave a boron-to-silicon molar ration of 4·28. As the boron-to-silicon ratio increases in the reaction mixture (examples 3 and 4), B_6Si formation is favoured. It appears that a low boron-to-silicon ratio (1:1 or less) and temperatures less than 1370° are required to form B_4Si only.§

As the reaction temperature is increased over 1370°, B_6Si formation is favoured.

§ Added in proof: after this paper was submitted, C. BROSSET and B. MAGNUSSON, *Nature, Lond.* **187**, 54 (1960), showed that B_4Si free of B_6Si could be prepared from the stoichiometric mixture heated at 1200° for about three weeks in argon.

[18] J. I. WATTERS and R. DEWITT, *J. Amer. Chem. Soc.* **82**, 1333 (1960).

At 1430° in 2 hr (example 6), B_6Si is the only phase observed. Large boron-to-silicon ratios in the reactants favour B_6Si formation (examples 7–10), and it was possible to demonstrate the stoichiometric reaction from the elements (example 11).

One experiment (example 12) was carried out with 91 atomic per cent of boron and 9 atomic per cent of silicon as reactants at 1430° in helium atmosphere because previous work[14] indicated that a reaction product (at unspecified temperature) of 95 atomic per cent of boron and five atomic per cent of silicon gave an X-ray pattern showing no silicon and an unidentified product. Visual examination of the present reaction product showed a black, inner core, characteristic of reacted boron–silicon mixtures. X-ray examination of this product indicated the presence of much amorphous material (boron) as well as the presence of B_6Si. Only one X-ray line attributable to silicon was observed.

One experiment (example 13) was carried out in hydrogen (molybdenum furnace) at 1710°. Here, silicon was found as the major constituent with B_6Si as the minor component.

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Along with the formation of boron silicides in the reaction of the elements, there is observed the formation of a solid solution of boron and/or boron silicide (B_4Si or B_6Si, depending upon the reaction temperatures employed) in silicon. The question of the solubility of boron in silicon has recently been investigated by SLEPTSOV and SAMSONOV[19] who showed that the solubility is 1·20 atomic per cent at room temperature and increases to 2·9 atomic per cent at 1300°. The lattice parameter of silicon with 2·9 atomic per cent boron is 5·41 Å, according to their plot. Some experiments were carried out at 1370° in stagnant air with silicon-to-boron molar ratios of 4, 6, 8 and 10:1. X-rays results of the reaction product showed the presence of B_4Si and silicon, the latter with a reduced cell size. The lattice parameter of the silicon after reaction was calculated to be 5·418 Å, in close agreement with previous findings[19] for the solubility of boron in silicon at 1300°.

DISCUSSION

The numerous workers who attempted to prepare boron silicide previously probably missed its detection either because the X-ray powder patterns of B_6Si and B_4Si were not available for substantiation of the reaction products or because synthesis temperatures employed were too high. The powder pattern for B_6Si is complex and somewhat similar to that of crystalline boron.[20,21] Furthermore, the presence in the reaction product of a strongly diffracting substance such as silicon tends to mask the B_6Si pattern, making identification of the latter difficult. A previous study[4] pointed out, "The powder patterns (of the reaction product of silicon and boron at 1725°) showed strong lines of a pure silicon-metal phase with some weak lines possibly due to boron."

As far as reaction temperatures are concerned, it has been shown that boron silicide (B_4Si) will form as low as 1210°, in contrast with all previous attempts where temperatures of 1400° or higher were employed. Fusion conditions are not required. In fact, the reaction to form both B_4Si and B_6Si occurs in the solid state.

Acknowledgements—The co-operation of Mrs. M. J. CASSIDY and Dr. C. H. ARMITAGE in X-ray assistance is gratefully acknowledged.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 112 to 119. Pergamon Press Ltd.

ADDITION COMPOUNDS OF METHYL SUBSTITUTED CYCLIC ETHERS WITH BORON TRIFLUORIDE[1]

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(*Received* 18 *February* 1960; *in revised form* 4 *August* 1960)

Abstract—A manometric method was used to study the addition compounds of boron trifluoride with 2-methyltetrahydrofuran, 2,5-dimethyltetrahydrofuran, 2-methyltetrahydropyran and 2,6-dimethyltetrahydropyran. Physical characteristics are given. Methyl substitution in both tetrahydrofuran and tetrahydropyran causes the addition compound to be more highly dissociated, with the effect being much more pronounced for the latter. In spite of the increased dissociation, the addition compounds formed with the substituted five-membered ring ethers have higher enthalpies and entropies of dissociation than does that formed with the unsubstituted ether. In the six-membered ring system, however, all the thermodynamic values for the dissociation process are largest for the unsubstituted case.

STUDIES of the boron trifluoride addition compounds with tetrahydrofuran and tetrahydropyran indicate that the ring size effect rather than steric interaction between the boron trifluoride and the α-methylene hydrogen atoms of the cyclic ether seems to be the major factor in accounting for the relative stability of the two complexes,[2] namely, tetrahydrofuran : boron trifluoride > tetrahydropyran : boron trifluoride. Even methyl substitution on the α-carbon atom in the cyclic ethers does not produce steric interference in the formation of hydrogen bonds with chloroform or methanol-d,[3] since the normal inductive effect is observed. The same is true in complex formation of 2-methyltetrahydrofuran with the more bulky iodine as compared to tetrahydrofuran itself.[4,5] With a still more bulky acid it is very possible that methyl substitution could cause the steric or "F-strain" effect to overshadow the inductive effect. A quantitative answer to this question was sought by investigating the influence of α-methyl substituents on the strength of the linkage and stability of the addition compounds formed between boron trifluoride and the five- and six-membered ring ethers. It is clear that in the absence of steric effects in the α-methyl substituted cyclic ethers it would not be possible to invoke "F-strain" as arising from the interaction of boron trifluoride with the α-methylene groups in the unsubstituted cyclic ethers.

EXPERIMENTAL

Materials. The boron trifluoride was the same as that described previously,[6] and the 2-methyltetrahydrofuran was purified as described elsewhere.[4] Synthesis and purification of the other compounds are described below. The purity of each cyclic ether was checked by gas phase chromatography.

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(6) D. E. McLAUGHLIN and M. TAMRES, *J. Amer. Chem. Soc.* **82**, 5618 (1960).

2-Methyltetrahydropyran was prepared by the condensation of 1,3-dibromopropane with acetoacetic ester in the presence of two moles of sodium ethoxide, yielding ethyl 2-methyl-5,6-dihydropyran-3-carboxylate, which was hydrolysed and decarboxylated.[7] The resulting 2-methyl-5,6-dihydropyran was distilled over sodium (b.p. 105–106° (reported 106°[7]), yield 38%) and reduced by hydrogen at 800 lb/in² over Raney nickel at 110°, to give 75 per cent of 2-methyltetrahydropyran, b.p. 100–101° (740 mm), (reported b.p. 103–104° at 720 mm).[7] The dehydration of 1,5-hexanediol with sulphuric acid[7] gave a product of about the same boiling point, but it was shown by gas phase chromatography to be a mixture of two compounds in approximately 60:40 ratio. It is believed that rearrangement occurred to give 2,5-dimethyltetrahydrofuran to a considerable extent.

TABLE 1.—SATURATION PRESSURES OF 2-METHYLTETRAHYDROFURAN:BORON TRIFLUORIDE

m.p. −28·8 – −27·3°C

Saturation pressure equation (liquid):

$$\log P = \frac{-3291}{T} + 10{\cdot}243$$

Temperature (°C)	50·5	55·0	59·9	65·5	70·1
Pressure (mm)	1·17	1·59	2·29	3·37	4·59
Temperature (°C)	74·9	79·9	85·1	89·8	94·6
Pressure (mm)	6·20	8·41	11·41	15·01	19·55

2,6-Dimethyltetrahydropyran was prepared by a synthetic sequence analogous to that above, starting with 1,3-dibromobutane and acetoacetic ester.[8] The product, obtained in 49 per cent yield, had b.p. 110° (735 mm), n_{20}^{D} 1·4172. This material has been synthesized previously by different methods and reported to have b.p. 113·5–115°,[9] 115–117°[10] and 118°[9], the first being probably the *cis* compound, the last the *trans* and the second a mixture of both. Because of the method of reduction and the stable di-axial configuration for the *cis* isomer, our product is presumed to be *cis* or mostly *cis*.

2,5-Dimethyltetrahydrofuran was prepared by hydrogenation of 2,5-dimethylfuran over platinum oxide catalyst at room temperature and 1–2 atmospheres pressure. It had b.p. 91–92° (740 mm). Previous workers have reported b.p. 89–91°,[11] 90·5–91·0°,[12] 92°,[13] 95°[14] and 96°[15] and n_{20}^{D} 1·4032,[14] 1·4043[12] and 1·405[13] for products which were probably mixtures of the *cis* and *trans*-isomers. Because of the mild conditions for hydrogenation used here, our product is presumed to be the *cis* isomer.

Apparatus. The manometric unit used in this investigation has been described previously.[6]

RESULTS

2-Methyltetrahydrofuran:boron trifluoride. Boron trifluoride and 2-methyltetrahydrofuran interact to form a stable 1:1 addition compound which is a colourless liquid at room temperature but a white solid at low temperatures. The compound melts at −28·8 – −27·3°, lower than that (11·7–12·3°) for the compound formed with tetrahydrofuran. The saturation pressures in the range studied were slightly greater at corresponding temperatures than those of tetrahydrofuran:boron trifluoride. These data can be found in Table 1 and Fig. 1.

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[8] R. G. FARGHER and W. H. PERKIN, *J. Chem. Soc.* **105**, 1353 (1914).
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Dissociation pressure data for this addition compound can be found in Table 2 and Fig. 2.

2-Methyltetrahydropyran:boron trifluoride. Boron trifluoride interacts with 2-methyltetrahydropyran to form a colourless liquid 1:1 addition compound at room temperature. The compound is a white solid at low temperatures and melts at −7–−6°, which is lower than that (9·5–10·2°) for the addition compound formed with

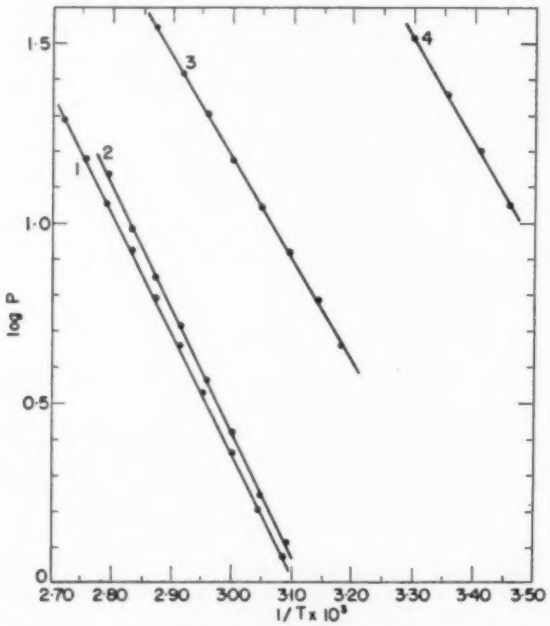

Fig. 1.—Saturation pressure data for the metyhl substituted cyclic ether:boron trifluoride addition compounds.
1. 2-Methyltetrahydrofuran:boron trifluoride (liquid)
2. 2,5-Dimethyltetrahydrofuran:boron trifluoride (liquid)
3. 2-Methyltetrahydropyran:boron trifluoride (liquid)
4. 2,6-Dimethyltetrahydropyran:boron trifluoride (solid).

tetrahydropyran. The saturation pressures were greater at corresponding temperatures than those for tetrahydropyran:boron trifluoride. These data can be found in Table 3 and Fig. 1.

Dissociation pressure data for this addition compound can be found in Table 4 and Fig. 2.

2,5-Dimethyltetrahydrofuran:boron trifluoride. The addition compound of boron trifluoride with 2,5-dimethyltetrahydrofuran is a white solid at temperatures somewhat below room temperature and melts to give a colourless liquid. The observed melting point is 23–24°. Some instability of this addition compound was observed in the gas phase studies above 100°, but no decomposition of the material at room temperature was noted over periods of several days. In making saturation pressure measurements, it was observed that prolonged heating at 120° resulted in an increase in the apparent saturation pressures in the temperature range 50–90°. Saturation pressures taken without subjecting the compound to temperatures above 90° are

TABLE 2.—DISSOCIATION DATA FOR 2-METHYLTETRAHYDROFURAN:BORON TRIFLUORIDE

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
8·230 mm BF_3 and 8·434 mm 2-methyltetrahydrofuran at 0°C $\log K = \frac{-3921}{T} + 8{\cdot}892$		
96·2	18·672	0·0187
100·0	19·337	0·0243
104·9	20·112	0·0328
109·8	20·893	0·0452
114·9	21·585	0·0599
119·8	22·285	0·0828
124·9	22·886	0·109
7·947 mm BF_3 and 8·103 mm 2-methyltetrahydrofuran at 0°C $\log K = \frac{-3873}{T} + 8{\cdot}757$		
95·1	17·848	0·0172
99·9	18·658	0·0239
104·9	19·420	0·0326
104·9	19·431	0·0328
109·8	20·185	0·0453
114·9	20·830	0·0594
119·8	21·445	0·0785
124·5	22·017	0·104
130·7	22·687	0·148

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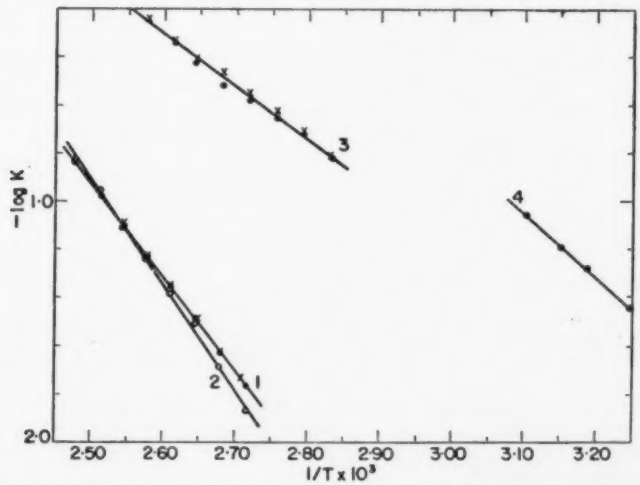

FIG. 2.—Log K vs. $1/T$ for the methyl substituted cyclic ether:boron trifluoride addition compounds.

1. × 8·434 mm 2-methyltetrahydrofuran and 8·230 mm BF_3
   ● 8·103 mm 2-methyltetrahydrofuran and 7·947 mm BF_3
2. ○ 8·323 mm 2,5-dimethyltetrahydrofuran and 8·216 mm BF_3
3. ● 12·936 mm 2-methyltetrahydropyran and 12·537 mm BF_3
   × 15·156 mm 2-methyltetrahydropyran and 15·411 mm BF_3
4. ● 13·300 mm 2,6-dimethyltetrahydropyran and 14·094 mm BF_3

Table 3.—Saturation pressures of 2-methyltetrahydropyran:boron trifluoride

m.p.: −7 – −6°C

Saturation pressure equation (liquid):

$$\log P = \frac{-2809}{T} + 9{\cdot}608$$

Temperature (°C)	41·0	45·0	50·0	55·0	60·1
Pressure (mm)	4·61	6·13	8·31	11·16	14·96
Temperature (°C)	65·1	69·7	75·0		
Pressure (mm)	20·11	26·06	35·16		

Table 4.—Dissociation data for 2-methyltetrahydropyran:boron trifluoride

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
12·537 mm BF_3 and 12·936 mm 2-methyltetrahydropyran at 0°C		
	$\log K = \frac{-2107}{T} + 5{\cdot}149$	
79·8	31·057	0·151
84·8	31·791	0·191
89·7	32·418	0·223
94·5	33·109	0·260
99·7	33·615	0·300
105·2	34·320	0·381
109·5	34·853	0·459
15·411 mm BF_3 and 15·156 mm 2-methyltetrahydropyran at 0°C		
	$\log K = \frac{-2167}{T} + 5{\cdot}344$	
80·1	37·000	0·158
84·8	37·921	0·198
89·7	38·731	0·239
94·7	39·486	0·281
99·7	40·296	0·348
104·7	40·972	0·395
109·5	41·679	0·475
115·0	42·460	0·580

Table 5.—Saturation pressures of 2,5-dimethyltetrahydrofuran:boron trifluoride

m.p.: 23–24°C

Saturation pressure equation (liquid):

$$\log P = \frac{-3419}{T} + 10{\cdot}678$$

Temperature (°C)	50·2	54·8	59·9	64·8	69·9
Pressure (mm)	1·30	1·75	2·62	3·68	5·22
Temperature (°C)	74·8	79·9	84·8	89·8	
Pressure (mm)	7·11	9·66	13·72	18·20	

given in Table 5 and Fig. 1. Again they are higher at comparable temperatures than those of either tetrahydrofuran:boron trifluoride[2] or 2-methyltetrahydrofuran:boron trifluoride.

In the dissociation studies, the onset of an irreversible reaction was noted by the slow change in the dissociation constant with time at a given temperature. The change was sufficiently slow to permit accurate determination of the dissociation data. These are presented in Table 6 and Fig. 2.

2,6-*Dimethyltetrahydropyran:boron trifluoride.* The freshly prepared addition compound of 2,6-dimethyltetrahydropyran with boron trifluoride is a white solid at

TABLE 6.—DISSOCIATION DATA FOR 2,5-DIMETHYLTETRAHYDROFURAN:BORON TRIFLUORIDE

$$\log K = \frac{-4327}{T} + 9{\cdot}908$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
8·216 mm BF_3 and 8·323 mm of 2,5-dimethyltetrahydrofuran at 0°C		
95·0	17·887	0·0136
100·0	18·901	0·0206
105·0	19·885	0·0311
110·0	20·627	0·0417
115·0	21·388	0·0578
120·0	22·067	0·0783
124·9	22·757	0·112
130·6	23·365	0·151

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room temperature and melts in the range 28–35° to give a colourless liquid. This compound was observed to undergo decomposition at room temperature over a period of several days to give an amber coloured liquid. After fractionation of this liquid, a residue of a colourless, nonvolatile liquid remained which could not be moved in the vacuum line under high vacuum. The wide melting range of the freshly prepared compound could not be attributed to decomposition nor could it be attributed to an impure sample of the ether since gas phase chromatography had verified its purity. There is considerable dissociation of the vapour at the melting temperature, and perhaps the complex in the liquid state is also somewhat dissociated, a condition known to cause a wide melting range.[16] Another possible explanation is that the mixture of *cis* and *trans* isomers which are possible in such a disubstituted ring system is causing the wide melting range. Some saturation pressures of the freshly prepared addition compound are presented in Table 7 and Fig. 1.

In the interaction of boron trifluoride with 2,6-dimethyltetrahydropyran, a secondary, irreversible reaction occurred which was sufficiently rapid so that reliable dissociation data could be obtained only within the first one and a half hours after bringing the two components together, after which the pressure was observed to increase slowly for a short time and thereafter to decrease. A nonvolatile liquid residue remained in the reaction vessel which necessitated a thorough cleaning before further experimental work. Fortunately, the experimental apparatus of this investigation permitted rapid measurement of dissociation pressures, and it was possible to

[16] A. FINDLAY, *The Phase Rule and Its Applications* (9th Ed.) p. 145. by A. N. CAMPBELL and N. O. SMITH, Dover, New York (1951).

obtain several measurements at various temperatures before the onset of the secondary reaction. The dissociation data for this addition compound can be found in Table 8 and Fig. 2.

DISCUSSION

The thermodynamic values derived from the dissociation data are summarized in Table 9. The values for tetrahydrofuran:boron trifluoride and tetrahydropyran:boron trifluoride are included[2] for purposes of comparison. The larger experimental errors assigned to the thermodynamic values for 2,5-dimethyltetrahydrofuran and

Table 7.—Saturation pressures of 2,6-dimethyltetrahydropyran:boron trifluoride

m.p.: 28–35°C.
Saturation pressure equation (solid):

$$\log P = \frac{-2861}{T} + 10{\cdot}957$$

Temperature (°C)	15·8	20·0	24·9	30·0
Pressure (mm)	11·4	16·0	23·1	33·0

Table 8.—Dissociation data for 2,6-dimethyltetrahydropyran:boron trifluoride

$$\log K = \frac{-2610}{T} + 7{\cdot}045$$

Temperature (°C)	Pressure (mm)	Dissociation constant K (atm)
14·094 mm BF_3 and 13·300 mm 2,6-dimethyltetrahydropyran at 0°C		
34·6	26·382	0·0364
40·2	27·797	0·0529
44·1	28·569	0·0649
49·1	29·585	0·0884

2,6-dimethyltetrahydropyran are due to the experimental difficulty with irreversible reaction which was encountered for these two cases, particularly the latter.

The thermodynamic data of Table 9 show that methyl substitution on the α-carbon atoms of the five-membered ring ether results in a higher enthalpy of dissociation for the addition compound with boron trifluoride. If the enthalpy value is taken as a measure of the strength of interaction between boron trifluoride and the ether, its increase with methyl substitution must reflect an increased electron density on the oxygen atom due to the normal inductive effect.

This enhancement of electron donor ability upon α-methyl substitution has been reported in hydrogen bonding studies on the cyclic ethers.[3] A more quantitative measure of the effect can be made by comparing the iodine complexes with tetrahydrofuran and with 2-methyltetrahydrofuran.[4,5] The thermodynamic values for dissociation of the former are $\Delta H^\circ = 5{\cdot}3$ kcal/mole, $\Delta F^\circ_{25} = 1{\cdot}70$ kcal/mole, and $\Delta S^\circ = 11{\cdot}6$ e.u., while those for the latter are $\Delta H^\circ = 6{\cdot}2$ kcal/mole, $\Delta F^\circ_{25} = 1{\cdot}84$ kcal/mole, and $\Delta S^\circ = 14{\cdot}6$ e.u. In these studies, where steric effects were judged to be small, there is an increase in all the thermodynamic functions.

However, this is not the case for the boron trifluoride addition compounds of the cyclic ethers studied here. Introduction of one methyl group in the five-membered ring ether causes about 1 kcal increase in $\Delta H°$ but about a 0·4 kcal decrease in $\Delta F°$, while in the six-membered ring ether the corresponding change causes a decrease in both $\Delta H°$ and $\Delta F°$, amounting to 5·6 and 1·7 kcal, respectively. This, of course, points to the presence of steric repulsive forces in the addition compounds, and there is similarity to the case of acyclic ethers, in which $\Delta F°$ decreases by 0·6–0·9 kcal per α-methyl group in the series: methyl ether, ethyl ether, isopropyl ether.[17]

TABLE 9.—THERMODYNAMIC DISSOCIATION DATA FOR ADDITION COMPOUNDS OF METHYL SUBSTITUTED CYCLIC ETHERS WITH BORON TRIFLUORIDE

	$\Delta H°$ (kcal/mole)	K_{100} (atm)	$\Delta F°_{100}$ (cal/mole)	$\Delta S°$ (e.u.)
Tetrahydrofuran:BF_3	16·80 ± 0·2	0·0144	3145 ± 20	36·6 ± 0·6
2-Methyltetrahydrofuran:BF_3	17·83 ± 0·2	0·0241	2763 ± 20	40·4 ± 0·6
2,5-Dimethyltetrahydrofuran:BF_3	19·80 ± 0·5	0·0206	2879 ± 40	45·3 ± 1·5
Tetrahydropyran:BF_3	15·42 ± 0·2	0·0339	2510 ± 20	34·6 ± 0·6
2-Methyltetrahydropyran:BF_3	9·78 ± 0·3	0·332	818 ± 30	24·0 ± 0·9
2,6-Dimethyltetrahydropyran:BF_3	11·9 ± 1	1·13	−87 ± 80	32·2 ± 3

In the five-membered ring, apparently the steric repulsion is small enough to permit the approach of the boron atom close enough for strong interaction, only with a very restricted orientation of the two species relative to each other. This is reflected in the large increase in the entropy of dissociation. In the six-membered ring, however, the α-methyl group gives considerably more interference so that no such rigid orientation is possible—only a weak association with considerably more freedom in each of the species than in the unsubstituted case.

In each ring size, introduction of the second methyl group at the other α-carbon atom caused an increase of about 2 kcal in the interaction with boron trifluoride, compared to the monomethyl derivative, and also an increase in entropy was observed for each. This would imply that the steric repulsion was less than the electronic advantage for the second methyl group, so that a stronger association with greater rigidity resulted. Further comparison is difficult because at least one of these compounds was probably a mixture of *cis* and *trans* isomers, which probably interact somewhat differently with boron trifluoride.

Acknowledgements—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgement is hereby made to the donors of said fund. One of us (D. E. M.) wishes to express his appreciation to both the Horace H. Rackham School of Graduate Studies of The University of Michigan and the Allied Chemical Corporation for fellowships.

[17] H. C. BROWN and R. M. ADAMS, *J. Amer. Chem. Soc.* **64**, 2557 (1944).

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 120 to 124. Pergamon Press Ltd.

ETHYLENEDIAMINE ADDITION COMPOUNDS OF METAL PERCHLORATES

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(*Received* 26 *January* 1960; *in revised form* 2 *August* 1960)

Abstract—The ethylenediamine addition compounds of the perchlorates of lithium, magnesium, calcium, strontium, barium, copper and zinc were prepared by the direct union of ethylenediamine and the corresponding metal perchlorate. The thermal stabilities of these compounds were studied by differential thermal analysis and thermogravimetric analysis methods.

THE anhydrous perchlorates of the alkaline earth metals are excellent absorbents for water and for ammonia. In this work there is reported additional compounds of alkaline earth perchlorates with ethylenediamine (en).

The addition compounds of the alkaline earth perchlorates and ammonia have already been studied[1] and their composition shown to vary with the conditions of temperature and pressure owing to the relatively high vapour-pressure of the ammonia over the compounds. Because of the lower volatility of ethylenediamine and because of the formation of chelate rings, addition compounds of it and the alkaline earth perchlorates might be expected to be more stable than the corresponding ammonia compounds.

The combination in a single molecule of a combustible, organic component, a potentially powerful oxidant, and a flame colouring agent should give to such compounds some startling properties.

EXPERIMENTAL

Reagents. The alkaline earth perchlorates used were reagent grade chemicals obtained from the G. Frederick Smith Chemical Company, Columbus, Ohio. Anhydrous ethylenediamine was purified by distillation. The copper and zinc perchlorate hexahydrates were prepared by treating an excess of the corresponding carbonate with 70 per cent perchloric acid, filtering, crystallizing, filtering and finally recrystallizing from water.

Preparation. In general the ethylenediamine derivatives were prepared by the careful addition of the anhydrous metal perchlorate to an excess of ethylenediamine with stirring. The reactions were exothermic and caution was taken to avoid spattering. It was not necessary to obtain complete dissolution. The mixture was cooled to room temperature and the precipitate washed by decantation with 1:10 ethanol-ethyl acetate to remove the excess ethylenediamine. The material was sucked dry and dried under reduced pressure over anhydrous magnesium perchlorate. Some necessary variations in individual cases are described in detail below.

$LiClO_4 \cdot 2en$. Anhydrous lithium perchlorate was placed in a vacuum desiccator over ethylenediamine and permitted to absorb the vapour until the material became pasty. The product was washed twice with ethyl acetate. It was then dissolved in ethyl acetate by warming to 50°. The solution was filtered. On cooling a white crystalline compound precipitated which was filtered off, recrystallized from ethyl acetate again and dried under reduced pressure over anhydrous magnesium perchlorate.

In some preparations the initial absorption process was allowed to proceed until complete solution resulted; crystallization of the addition compound from the ethyl acetate could not then be achieved.

[1] G. F. SMITH and E. G. KOCH, *Z. Anorg. Chem.* **223**, 17 (1935).

Ethanol was avoided in the washing operation as early experience showed the addition compound could not be recovered.

$Mg(ClO_4)_2 \cdot 3en$. This compound was prepared in the same manner as the lithium compound except that 1 : 10 ethanol-ethyl acetate was used as the wash solution. The general method of preparation failed to give a homogeneous product.

$Ca(ClO_4)_2 \cdot 4en$; $Sr(ClO_4)_2 \cdot 4en$; $Ba(ClO_4)_2 \cdot 4en$; $Cu(ClO_4)_2 \cdot 2{\cdot}5en$; $Zn(ClO_4)_2 \cdot 3en$. These compounds were all prepared by the general method described above. The hexahydrates rather than the anhydrous perchlorates were used to prepare the zinc and copper compounds.

TABLE 1.—SUMMARY OF ANALYTICAL RESULTS
(en = ethylenediamine)

Compound	Metal		Perchlorate calcd.* (%)	Amine		Total (%)
	Theor. (%)	Exp. (%)		Theor. (%)	Exp. (%)	
$LiClO_4 \cdot 2en$	3·06	3·002	43·03	53·00	52·16	98·19
$Mg(ClO_4)_2 \cdot 3en$	6·032	6·034	49·38	44·64	44·17	99·75
$Ca(ClO_4)_2 \cdot 4en$	8·35	8·38	41·60	50·11	49·98	99·96
$Sr(ClO_4)_2 \cdot 4en$	16·63	16·62	37·75	45·57	45·21	99·58
$Sr(ClO_4)_2 \cdot 2en$	21·55	21·61	49·06	29·51	28·83	99·50
$Ba(ClO_4)_2 \cdot 4en$	23·85	23·70	34·32	41·64	41·54	99·56
$Cu(ClO_4)_2 \cdot 2{\cdot}5en$	15·41	15·32	47·99	36·40	36·55	99·86
$Zn(ClO_4)_2 \cdot 3en$	14·71	14·76	44·94	40·50	40·48	100·18

* Calculated from the metal analysis.

$Sr(ClO_4)_2 \cdot 2en$. Strontium ethylenediamine perchlorate was heated at 165–170° in a stream of heated, dry air for 1 hr. The liquid so obtained solidified on cooling and could be cast into sticks of considerable physical strength.

Analysis. Ethylenediamine was determined by titration of a water solution of the compound with standard hydrochloric acid using methyl purple indicator. For the copper compound it was necessary to determine the end-point potentiometrically because of the colour of the copper amine. Owing to the insolubility of the magnesium compound, it was dissolved in an excess of standard hydrochloric acid and back titrated with standard alkali.

Magnesium, calcium, strontium, barium and zinc were determined by titration with EDTA using Eriochrome Black T as indicator. A small and known amount of magnesium was added to sharpen the end-point in the titrations of clacium, strontium and barium. Copper was determined by electrodeposition. Lithium was determined by passage of the aqueous solution of the sample through a column of IR–120, a strong cation exchange resin, in the hydrogen form and titration of the perchloric acid in the eluate with standard sodium hydroxide.

The analytical results are tabulated in Table 1.

Properties. The addition compounds were found to be remarkably hygroscopic, some gaining up to 66 per cent in weight of water in 24 hr on exposure to air saturated with moisture. The odour of ethylenediamine was noticed over the calcium, strontium and barium compounds only. All of the compounds proved readily soluble in water with the exception of the magnesium compound, the only alkaline earth compound which was not delinquescent; it was readily soluble in dilute acid.

All of the compounds were obtained white except for the copper compound which exhibited the characteristic, deep blue copper-ammine colour. There is some tendency for the white compounds to turn slightly yellow on standing although this varied from batch to batch and seemed to be a property of the ethylenediamine for compounds prepared from freshly distilled ethylenediamine were still white after four months.

All of the compounds burned with self-sustaining flames when ignited on a steel plate with a flame. They yielded the characteristic colours of the metal and considerable smoke. The vigour of this open-plate burning increased in the order calcium, zinc, magnesium, barium, strontium, lithium and copper. The copper compound burned with detonation of individual crystals.

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Differential thermal analysis (DTA). All of the compounds prepared with the exception of the copper compound were subjected to a differential thermal analysis study. The DTA apparatus used was that described by GORDON and CAMPBELL,[2] modified so that the temperature of the sample was obtained by a separate thermocouple; this resulted in greater stability by eliminating the interruption in the differential thermocouple circuit. The temperature of the sample was plotted directly on a Brown Electronic 3-channel, 50 mV full scale, point plotting recorder utilizing all three channels. The differential temperature was plotted on a Brown Electronic 12 mV full scale, strip chart recorder using a 28-gauge iron–constantan thermocouple. Sample temperature was related to the corresponding

TABLE 2.—DIFFERENTIAL THERMAL ANALYSIS OF ETHYLENEDIAMINE ADDITION COMPOUNDS

Compound	Endotherms (°C)	Exotherms (°C)	Decomposition (°C)
$LiClO_4 \cdot 2en$	95 (2)*	315	357
	268 (4)		
$Mg(ClO_4)_2 \cdot 3en$	110 (3)	326 (88)	326
	315 (6)		
$Ca(ClO_4)_2 \cdot 4en$	177 (12)	285 (45)	295
$Sr(ClO_4)_2 \cdot 4en$	168 (55)	293	317
	192 (11)		
$Ba(ClO_4)_2 \cdot 4en$	118 (1)	277	295
	176 (2)		
$Zn(ClO_4)_2 \cdot 3en$	142 (4)	270 (47)	275

* The temperature in parenthesis is the temperature deviation from the apparent base line for the corresponding endotherm or exotherm. The absence of this value indicates the data was not available as the decomposition was accompanied by an explosion which terminated the run.

points on the differential temperature plot by utilizing the built-in microswitch of the point plotting recorder; each time a point was plotted on the sample temperature curve, the microswitch opened causing a slight kick in the differential temperature plot. Thermocouples were checked with standard melting point samples of tin and zinc and with boiling water. The temperature was increased linearly throughout the temperature range used and was accurate to within 2°, the recorded reading always being high.

The operation of the DTA apparatus was checked by a run on silver nitrate which GORDON and CAMPBELL reported as having marked deflexions in the expected range of the ethylenediamine addition compounds. Of the six temperatures at which deflexions were noted on the curve reported by GORDON and CAMPBELL, acceptable agreement was obtained at two and exact agreement at the other four.

Efforts were made to keep the size of the particles, the size of the sample, packing and positioning as uniform as possible. The hygroscopicity of the compounds required that the work be done quickly but even so the absorption of water did cause some shifting of the DTA base line. Calculations were made from the new or apparent base line. The results are summarized in Table 2.[3]

Thermogravimetric analysis. The thermobalance used was an equal-arm balance converted to positive displacement and direct reading by the variable transformer–electronic arrangement of GORDON and CAMPBELL.[4] The temperature of the sample was recorded on a Brown Electronic 3-channel point plotting recorder. The output of the demodulator was fed into a Brown Electronic strip chart recorder. The temperature of the sample was manually transferred to the thermogravimetric curve as the analysis proceeded. The recorder was found to be linear throughout the 200 mg range used, the greatest source of error being the reading of the chart. Again, owing to the hygroscopicity of the materials being studied, some initial drift (gain in weight) was recorded and the actual weight of the sample was taken as that during the linear portion at 100° at which time the apparatus had equilibrated and no true weight loss had yet resulted.

The results are summarized in Table 3.[3]

[2] S. GORDON and C. CAMPBELL, *Analyt. Chem.* **27**, 1102 (1955).
[3] The actual DTA and TGA curves obtained will be found in the Master of Science Thesis of H. W. WHARTON, The Library, Iowa State University. Ames, Iowa, (1958).
[4] S. GORDON and C. CAMPBELL, *Analyt. Chem.* **29**, 298 (1957).

RESULTS AND DISCUSSION

The composition of the addition compounds is about that expected: two molecules of ethylenediamine adding to the lithium salt, three to magnesium and zinc, and four to the alkaline earths. The figure of 2·5 for copper is interesting as further evidence of the great difficulty of forcing copper(II) to be hexacovalent.

Most inorganic compounds undergo thermal decomposition with definite losses in weight at specific temperatures and exhibit wide temperature regions of stability. The metal ethylenediamine perchlorates, however, exhibit a gradual, nearly linear loss

TABLE 3.—THERMOGRAVIMETRIC ANALYSIS OF ETHYLENEDIAMINE ADDITION COMPOUNDS

Addition Product	Decomposition temperature (°C)	Equivalent mol. wt. loss (en = 60)	No. of en lost at decomposition
$LiClO_4 \cdot 2en$	308	61·0	1
$Mg(ClO_4)_2 \cdot 3en$	327	60·5	1
$Ca(ClO_4)_2 \cdot 4en$	288	122	2
$Sr(ClO_4)_2 \cdot 4en$	323	200	3
$Ba(ClO_4)_2 \cdot 4en$	305	188	3
$Zn(ClO_4)_2 \cdot 3en$	258	29·6	0·5

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in weight throughout the heating and the endotherms obtained in the DTA studies were unusually broad and rather poorly defined. Together these indicate that ethylenediamine is released gradually on heating until the final explosive decomposition temperature is reached. Primarily of course, this is a matter of the conditions of the experiment; were the rate of heating sufficiently slow and a constant atmosphere maintained above the compounds, equilibrium and definite composition could be obtained but this would defeat the very purpose and design of the DTA and thermogravimetric methods. That equilibrium and definite composition can be achieved is evident from the one study made in this direction, the preparation of the strontium diethylenediamine compound.

The decomposition temperatures obtained by the two methods for any one compound agree about as well as can be expected in view of the difference in rate of heating. For all of the compounds the decomposition temperatures fall in the range 258–357°. Ethylenediamine perchlorate decomposes violently in this same range,[5] at 280°. The vigour of the final decomposition depends on the composition of the compound at that point. Those compounds bearing only one molecule of ethylenediamine as they reached the decomposition temperature explode: lithium, strontium and barium. The final decomposition of the zinc perchlorate, bearing 2·5 molecules of ethylenediamine at that point, is not explosive.

$LiClO_4 \cdot 2en$. The DTA curve showed primarily the difference in thermal conductivity of the material and the inert reference material. A shift in the base line resulted from the increased thermal conductivity of the molten material, for this compound melted at about 75°. An endotherm at 270° corresponded to the loss of one ethylenediamine prior to decomposition, the loss in weight starting at 120° and continuing until the decomposition temperature. Both curves terminated at the decomposition temperature. The explosion at the decomposition temperature was the most violent

[5] K. A. HOFFMAN, K. HOBOLD and F. QUOOS, *Liebigs Ann.* **396**, 314 (1912).

of any of the compounds studied. Only one molecule of ethylenediamine was present at this point.

$Mg(ClO_4)_2 \cdot 3en$. The DTA and thermogravimetric data indicated only the loss of one ethylenediamine at the decomposition temperature. The decomposition took place with the very rapid evolution of heat, white smoke and white flame; because no explosion occurred, it was possible to follow the DTA beyond the decomposition temperature. The light gray residue showed the presence of chloride and oxide.

$Ca(ClO_4)_2 \cdot 4en$. The gradual and nearly linear loss of weight began at 125°corresponding to the endotherm beginning at about 140°. This corresponded to the abrupt loss of the first molecule of ethylenediamine, tailing off as the second was lost prior to decomposition. The correspondingly smaller exotherm at decomposition compared with that of the magnesium compound was confirmed by the less vigorous decomposition. Chloride and oxide were found in the brownish residue.

$Sr(ClO_4)_2 \cdot 4en$. The DTA curve for this compound was as spectacular as its final decomposition. The endotherm at 165° corresponded in part to the loss of two molecules of ethylenediamine as shown by the preparation of the diethylenediamine compound by uniform heating of this compound at 165–170°C in a stream of heated, dry air. This endotherm tailed off to about 260° where the thermogravimetric data indicated that all of the second ethylenediamine had been released. The decomposition at 317° was a violent explosion with brilliant scarlet fire and smoke.

$Ba(ClO_4)_2 \cdot 4en$. Information from the two curves correlated well. Only one molecule of ethylenediamine remained at the decomposition temperature and the decomposition occurred with an explosion.

$Zn(ClO_4)_2 \cdot 3en$. Repeated runs on the DTA of this compound gave a large base line shift up to 200°. Corresponding to this there was no weight loss up to about 225°. The first loss in weight corresponded to one-half molecule of ethylenediamine. Thus 2·5 molecules remained at decomposition. The decomposition was vigorous but not explosive. Chloride ion and oxide were present in the carbonaceous residue.

Acknowledgements—The authors wish to acknowledge indebtedness to the G. Frederick Smith Chemical Company, Columbus, Ohio, for gifts of chemicals and funds for the purchase of apparatus. They wish also to express their appreciation to Dr. F. J. LINDSTROM for the use of his thermobalance.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 125 to 129. Pergamon Press Ltd.

THE REACTION BETWEEN PHOSPHORUS TRIFLUORIDE-BORANE AND AMMONIA

THE SYNTHESIS OF TRIAMIDOPHOSPHORUS-BORANE, $(NH_2)_3PBH_3$

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Contribution from the Department of Chemistry of the University of Michigan*

(*Received* 14 *July* 1960)

Abstract—The reaction of unstable phosphorus trifluoride-borane and ammonia yields the new, stable compound, $(H_2N)_3PBH_3$.

A formal analogy between BH_3 and O is developed, and evidence is presented to indicate that the B—P bond is not broken during the ammonolysis of F_3PBH_3.

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DIBORANE and excess phosphorus trifluoride react slowly at room temperature under a pressure of 8 atm to give F_3PBH_3 as the primary product.[1] The base displacement reaction between F_3PBH_3 and trimethylamine can be summarized by the equations:[1]

$$(CH_3)_3N + F_3PBH_3 \rightarrow (CH_3)_3NBH_3 + F_3P \quad (1)$$

$$F_3P + (CH_3)_3N_{(excess)} \rightarrow \text{Undefined products.}\dagger \quad (2)$$

It is tempting to extrapolate the behaviour of $N(CH_3)_3$ and to predict that a similar base displacement reaction might occur if ammonia were used as the base. On the other hand a well supported axiom of co-ordination chemistry indicates that the chemistry of ammonia can not be predicted from observations on trimethylamine. It was not suprising then to find in the original study[1] that ammonia reacts with F_3PBH_3 but no F_3P is liberated. An unidentified solid was obtained. A more proper description of the foregoing ammonia reaction is the subject of this paper.

The synthesis of $(H_2N)_3PBH_3$

When ammonia is allowed to react with F_3PBH_3 in diethyl ether over a gradually increasing temperature range from (−111–+25°C), the following process ensues:

$$6NH_3 + F_3PBH_3 \xrightarrow[-111-25°C]{Et_2O} 3NH_4F + (H_2N)_3PBH_3. \quad (3)$$

The product, triamidophosphorus–borane, is a new ether-soluble crystalline solid with a characteristic X-ray powder pattern. Its detailed structure has been worked out by NORDMAN[4] and its geometry is as expected from the above formula. It is stable (in dry air) when pure, but, like most borane compounds, its stability is

* This research was supported by the United States Air Force under Contract No. 33(616)-5874, monitored by the Chemistry Branch of the Aeronautical Research Laboratory, Wright Air Development Centre, Ohio.

† Although no definitive data on the F_3P—$N(CH_3)_3$ reaction products are available, GRIFFITHS and BURG[2] mention an unstable adduct at −78°C and HOLMES[3] has isolated a solid adduct of PCl_3 and $N(CH_3)_3$ at 0°C.

[1] R. W. PARRY and T. C. BISSOT, *J. Amer. Chem. Soc.* **78**, 1524 (1956).
[2] J. E. GRIFFITHS and A. B. BURG, *J. Amer. Chem. Soc.* **82**, 1508 (1960).
[3] R. R. HOLMES, *J. Amer. Chem. Soc.* **82**, 5285 (1960); *J. Phys. Chem.* **64**, 1295 (1960).
[4] C. E. NORDMAN, *Acta Crystalographica.* **13**, 535 (1960).

seriously reduced by small amounts of impurities. It is soluble in ethers, liquid ammonia and chloroform without decomposition, and dissolves in water with reaction, but the hydrogen evolution is slow unless the solution is acidified.

Observations on the mechanism of $(H_2N)_3PBH_3$ *formation*

In view of the high degree of dissociation of F_3PBH_3, particularly near room temperature, it was of some interest to determine whether the low temperature reaction was a direct ammonolysis, involving displacement of the fluorines of PF_3 by NH_2 groups, or whether the reaction proceeded in a more conventional fashion through a base displacement process involving the entire PF_3 molecule:

$$H_3N + F_3PBH_3 \rightarrow H_3NBH_3 + PF_3$$

$$PF_3 + 6NH_3 \rightarrow 3NH_4F + P(NH_2)_3$$

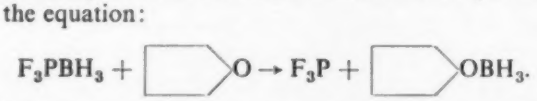
$$H_3NBH_3 + P(NH_2)_3 \rightarrow (H_2N)_3PBH_3 + H_3N$$

The first equation in the above sequence would be analogous to the reaction between trimethylamine and F_3PBH_3 [equation (1)]. A direct test of the postulated mechanism could be made by mixing H_3NBH_3, PF_3, and NH_3. If the reaction proceeded as described above, $(H_2N)_3PBH_3$ and NH_4F should appear as products. Experimentally it was found that no $(H_2N)_3PBH_3$ could be detected in the products and the original H_3NBH_3 could be recovered unchanged. These data support the postulate that the reaction proceeds through direct attack of NH_3 on F_3PBH_3 without initial rupture of the P—B bond.

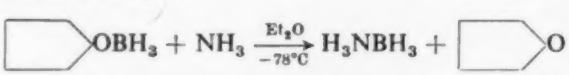
The role of reaction conditions

In the reaction of B_4H_{10} and B_2H_6 with ammonia it was found that direct attack of ammonia on the boron hydride gave a non-symmetrical cleavage of the double bridge bond, whereas a preliminary attack upon the boron hydride by a relatively strongly basic ether such as tetrahydrofuran, followed by a subsequent displacement of the ether with NH_3, resulted in a symmetrical cleavage product. A similar observation can be made involving F_3PBH_3 and NH_3.

At $-78°C$ no more than 15 per cent of the original F_3P was displaced from F_3PBH_3 by tetrahydrofuran over a $\frac{1}{2}$ hr period. These data support the earlier qualitative observation that the weak base, diethyl ether, does not displace F_3P at $-111°C$; (no visible evidence for dissoc.) hence, it is not unreasonable to postulate direct interaction between F_3PBH_3 and ammonia in diethyl ether at $-111°C$ or $-78°C$. On the other hand, F_3PBH_3 in tetrahydrofuran at $0°C$ is more than 90 per cent dissociated in accordance with the equation:



As expected, addition of ammonia to this solution, after PF_3 has been removed, gives a quantitative yield of N_3NBH_3.



In the original study[1] trimethylamine was allowed to react with F_3PBH_3 without any solvent. The formation of PF_3 and $(CH_3)_3NBH_3$ was observed just as in the low

temperature reaction in ether. On the other hand when ammonia was allowed to react with F_3PBH_3 *without solvent*, variable amounts of hydrogen gas were evolved and undefined solid and liquid products were obtained. Neither $(H_2N)_3PBH_3$ nor H_3NBH_3 could be detected in the products.

The reactions of F_3PBH_3 *and* F_3PO

It has been noted on many occasions that the BH_3 group is isoelectronic with the oxygen atom and indeed certain early molecular orbital arguments of MULLIKEN[5] compared BH_3 and the oxygen atom, and B_2H_6 and the oxygen molecule. While detailed physical analogies (e.g. magnetic properties, spectra, molecular energy levels, etc.) were rendered inapplicable by fundamental geometric differences resulting from the lower symmetry of the BH_3 group, it is tempting to examine the chemistry of certain BH_3 adducts to see if useful chemical correlations can be found between BH_3 and 0. It is immediately apparent that if PF_3 is used as a reference base, BH_3 is a much weaker acid than is the 0 atom; however, certain formalistic analogies still exist. The ammonia reaction is typical since it has been shown in this study that the reaction of F_3PO and NH_3 is comparable to that of F_3PBH_3 and NH_3 and may be written as:

$$6H_3N + F_3PO \rightarrow 3NH_4F + (H_2N)_3PO$$

The $(H_2N)_3PO$ is an ether insoluble white solid which is identical to the product prepared by KLEMENT and KOCH[6] from the ammonolysis of $POCl_3$. In a formal sense the analogy between F_3PBH_3 and F_3PO may be drawn. It may be profitably extended to other systems such as H_3BCO[7] for low temperature processes where the weaker acid strength of BH_3 does not introduce alternative complicating reactions.

EXPERIMENTAL

1. *Materials*

F_3PBH_3. This compound was prepared and purified using the literature method.[2]

Ammonia. Commercial reagent grade ammonia was dried and stored over sodium before use.

Ether. Solvents of the best grade were dried and stored over $LiAlH_4$ before use. All reactions were conducted in the vacuum system unless otherwise specified.

2. *The synthesis and characterization of* $(H_2N)_3PBH_3$

An ethyl ether solution of F_3PBH_3 at -111°C was frozen with liquid nitrogen and an excess of ammonia was condensed into a 20 mm reaction tube attached to the vacuum line. See Table 1 for typical data on quantities used. The temperature was then allowed to rise slowly with stops as follows: 2 hr at -111°C, 2 hr at -78°C, 5–6 hours at -35°C, and 2–7 days at 25°C. The tube was then opened; the ether solvent was distilled away, and the solid mixture of $(H_2N)_3PBH_3$ and NH_4F was separated by leaching the $(H_2N)_3PBH_3$ from the mixture with ethyl ether and/or liquid ammonia. When the reaction was carried out in liquid ammonia instead of ethyl ether, and the solid $(H_2N)_3PBH_3$ was extracted from the residue with liquid ammonia, yields of recovered product were high (92 per cent) but it was slightly yellow in colour, indicating lower purity. Analytical data were obtained on a purified sample for product characterization. (Found: hydridic hydrogen, 3·21; N, 45·5; B, 12·1. Calc. for $(H_2N)_3PBH_3$: hydridic hydrogen, 3·25; N, 45·23, B, 11·65%). A molecular weight of 98 was found in liquid ammonia solution. Calculated for $(H_2N)_3PBH_3$ is 92. Characterization of the product was completed by the single crystal X-ray study of NORDMAN[4] which gave an unequivocal structure.

[5] R. S. MULLIKEN, *Chem. Rev.* **41**, 207 (1947); *J. Chem. Phys.* **3**, 635 (1935).
[6] R. KLEMENT and O. KOCH, *Ber. Dtsch. Chem. Ges.* **87**, 333 (1954).
[7] J. C. CARTER and R. W. PARRY, Paper No. 22 presented before the Division of Inorganic Chemistry at the 137th National Meeting of the American Chemical Society. Cleveland, Ohio, April (1960).

Even if the initial ratio of NH_3 to PF_3BH_3 was one or less, no evidence for PF_3 liberation was ever detected; instead NH_4F was formed and *unreacted* F_3PBH_3 was recovered from the system.

It was noted that the reaction between NH_3 (in excess) and F_3PBH_3 to form $(H_2N)_3PBH_3$ is not complete at low temperatures. When the system was not allowed to warm above $-78°C$, the ratios of unrecovered ammonia to F_3PBH_3 ranged from 3·9 to 4·4. This suggests a formation of intermediate compounds $(H_2N)_2PFBH_3$ and $H_2NPF_2BH_3$.

$$F_3PBH_3 + 2NH_3 \rightarrow NH_4F + \mathit{H_2NPF_2BH_3}$$

$$H_2NPF_2BH_3 + 2NH_3 \rightarrow NH_4F + \mathit{(H_2N)_2PFBH_3}$$

Indeed, when the NH_4F precipitate was filtered out from such a reaction mixture, a clear ether solution could be obtained. From this solution a white precipitate, (NH_4F), formed again slowly when warmed to a higher temperature. Even if the mixture was kept at $-35°C$ for several hours, the product obtained after solvent removal was always contaminated with a viscous liquid which slowly decomposed to give a yellowish appearance, and the yield of purified $(H_2N)_3PBH_3$ was only 20–30 per cent on the basis of F_3PBH_3 used.

TABLE 1.—TYPICAL DATA FOR SYNTHESIS OF $(H_2N)_3PBH_3$

Reactants added			Materials recovered				
F_3PBH_3 (mmole)	NH_3 (mmole)	Ether (solvent) (ml)	NH_3 (mmole)	NH_4F (mmole)	H_2 (mmole)	$(H_2N)_3PBH_3$ (mmole)	Yield (%) $(H_2N)_3PBH_3$
1·05	6·040	5	*	*	0·024	0·837	82·4
2·70	25·99	10	10·88	6·72	0·077	2·020	75·0
1·70	0·5 ml liq.	0	*	3·78	0·018	1·570	92·0

* Not determined.

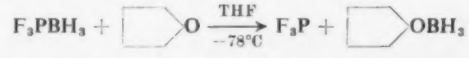
3. *The reaction between* H_3NBH_3, PF_3 *and* NH_3

In order to test a mechanism involving initial displacement of PF_3 by NH_3, followed by displacement of the NH_3 by newly formed $P(NH_2)_3$, the following reaction was carried out. One of two similar runs is described. A sample of H_3NBH_3 (0·709 mmole) was weighed into a reaction tube (volume = 50 cm³) equipped with a break-off tip. A 10 ml sample of diethyl ether was added then a quantity of PF_3 (0·782 mmole) was condensed into the system. When the reactor was allowed to warm up to $-78°C$, no external signs of reaction could be detected. After the system was again frozen with liquid nitrogen, an excess of ammonia was condensed into the reaction vessel and the tube was sealed. The temperature was raised stepwise as follows: $-111°C$ for 1 hr, $-78°C$ for ½ hour, 25°C for one week. When the tube was opened to the vacuum system, no H_2 was found; a mixture consisting of a solid precipitate of NH_4F (X-ray) and an unidentified compound of phosphorus was filtered off. [Ratio NH_3/F_3P consumed in one reaction was about 3·4 instead of the expected six for simple ammonolysis.] Ninety six per cent of the original H_3NBH_3 was recovered unchanged from the filtrate. It was identified as H_3NBH_3 on the basis of its X-ray powder pattern and by measurement of the H_2 produced on acid hydrolysis (1·285 mM H_2 from 13·4 mg sample; theory for H_3NBH_3 is 1·30 mM H_2).

4. *The system* F_3PBH_3*–tetrahydrofuran–ammonia*

a. *Low temperature* ($-78°C$). A sample of F_3PBH_3 amounting to 1·21 mmole was condensed into a reaction tube; then about 5 ml of tetrahydrofuran (THF) was condensed in by cooling with liquid nitrogen. The system was allowed to warm slowly to $-95°C$ and was maintained at that temperature for 1 hr. Pressure of the system was about 2 mm of Hg. The temperature was raised to $-78°C$ and maintained for ½ hr. The pressure remained constant at 6 mm Hg while the temperature was held at $-78°C$. The volatile components were distilled out at $-78°C$ and fractionated. A 1·01 mmole sample of undissociated F_3PBH_3, a PF_3 sample amounting to 0·180 mmole, and a trace

of a hydride (probably B_2H_6) which yielded 0·0545 millimole of H_2 on hydrolysis were obtained. The foregoing data indicate that the reaction



is no more than 15 per cent complete at −78°C under the conditions used. Such conditions are an order of magnitude more severe than those used in the diethyl ether study −(T = −111°C).

b. *High temperature* (0°C). A sample of F_3PBH_3 amounting to 1·01 mmole was condensed with about 5 ml of tetrahydrofuran; then the system was warmed to 0°C. To increase contact between vapour and liquid phases, the liquid was constantly agitated with a magnetically activated hopper type stirrer and the reactor was occasionally cooled with liquid nitrogen to condense the vapour into the liquid. After reaction for about 5 hr, the system was cooled to −78°C and volatile components were removed and fractionated. The first fraction consisted of 0·953 mmole of gas with a molecular weight of 88·4; the molecular weight for F_3P is 88·0. The second fraction amounted to 0·047 mmole of F_3PBH_3. A 3·49 mmole sample of NH_3 was introduced into the residual solution which had been held at −78°C. The solution was aged for 10 hr and filtered; then the solvent was distilled off. A sample of crude H_3NBH_3 weighing 31·7 mg (theoretical weight NH_3BH_3 based on F_3PBH_3 consumed is 29·8 mg) was recovered. The yield of purified product would be essentially quantitative. Apparently some ether still remained on the sample when it was weighed.

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5. *The reaction of* F_3PO *and* NH_3

F_3PO was prepared by fluorinating $POCl_3$ with commercial ZnF_2. The vapour-pressure of the F_3PO was determined; results are comparable to the literature values of TARBUTTON *et al.*[8]

A sample of F_3PO (1·546 mMole) and an 18·51 mmole sample of NH_3 were sealed in a tube with 10 ml of ethyl ether. A white solid formed quite rapidly, even at −111°C. After 3 days of standing at room temperature, the tube was opened and solid materials were filtered off. No solids could be recovered by evaporating the solvent from the filtrate.

The solid on the filtering disk was leached with liquid ammonia. NH_4F remained on the disk and $(H_2N)_3PO$ was obtained from the filtrate by evaporating the solvent ammonia. The yield was 79 per cent based on the F_3PO used. The $(H_2N)_3PO$ was identical to an authentic sample prepared from $POCl_3$ by the method of KLEMENT and KOCH.[6]

[8] G. TARBUTTON, E. P. EGAN, JR. and S. G. FRARY, *J. Amer. Chem. Soc.* **63**, 1872 (1941).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 130 to 134. Pergamon Press Ltd.

THE REACTIONS OF DINITROGEN TETROXIDE WITH LITHIUM CARBONATE WITH A SERIES OF MAGNESIUM COMPOUNDS, AND WITH ALUMINIUM CHLORIDE

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(*Received* 21 *July* 1960)

Abstract—The reactions of liquid dinitrogen tetroxide with lithium carbonate, basic magnesium carbonate, magnesium oxide, magnesium hydroxide, hydrated magnesium chloride, magnesium perchlorate and anhydrous aluminium chloride have been carried out. New methods for the preparation of anhydrous lithium nitrate and magnesium nitrate have been indicated. Evidence has been obtained for the formation of dinitrogen tetroxide adducts of magnesium nitrate and aluminium nitrate.

WE have recently been interested in the problem of the synthesis of new compounds possessing strong oxidizing characteristics and having low oxidation equivalent weights. Among the substances considered as possible interesting new species are complexes of light metal nitrates having ligands of relatively low molecular weight and high oxidizing capacity. We, therefore, have begun an investigation of such complexes of lithium nitrate, magnesium nitrate and aluminium nitrate. Since these nitrates are not commercially available in an anhydrous condition and since most of the hydrated nitrates are difficult to dehydrate, we have investigated the possible synthesis of these nitrates by means of the reactions of liquid dinitrogen tetroxide with various lithium and magnesium compounds. At the same time we have been interested in the formation of dinitrogen tetroxide adducts of these metal nitrates. Specifically, the reactions of dinitrogen tetroxide with lithium carbonate, magnesium carbonate, magnesium oxide, magnesium hydroxide, magnesium chloride hexahydrate, magnesium perchlorate and aluminium chloride, have been studied.

EXPERIMENTAL

Materials. Dinitrogen tetroxide supplied by the Matheson Company was purified by slow distillation through a 60 cm tube packed with a mixture of phosphorus (V) oxide and sand. It was stored at Dry-Ice temperature until ready for use. Chemically Pure or Reagent Grade lithium, magnesium and aluminium compounds were used throughout this study.

Procedure. The purification of the dinitrogen tetroxide and its reactions with the various lithium, magnesium and aluminium compounds were all carried out in an all glass apparatus which was fitted with Teflon plug stopcocks and Teflon sleeve joints. Fluorocarbon grease was used to lubricate ball joints. A diagram of the reaction apparatus is given in Fig. 1. A weighed sample of the metal compound was placed in Flask *A*, and an excess of dinitrogen tetroxide condensed over it from transfer cell *B*. The reflux condenser *C* was kept at 0°C to prevent the escape of dinitrogen tetroxide during the reaction period. Agitation in *A* was provided by a magnetic stirrer. At the end of the reaction period evaporation of excess dinitrogen tetroxide through trap *D* filled with Kel-F oil was permitted.

Analyses. Magnesium and aluminium were estimated by titration with ethylenediamine tetracetic acid solution using Eriochrome Black T as indicator. In the case of aluminium, an excess of ethylenediamine tetracetic acid solution was added and the excess back titrated with standard Zn^{2+}

solution. Total nitrogen was determined by Devarda's method, and chloride by the Volhard procedure. Nitrite was determined by oxidation with potassium permanganate. Karl Fischer reagent was used to estimate water content where such estimates were possible. Samples for X-ray diffraction and mulls for infra-red measurements were prepared in the dry box.

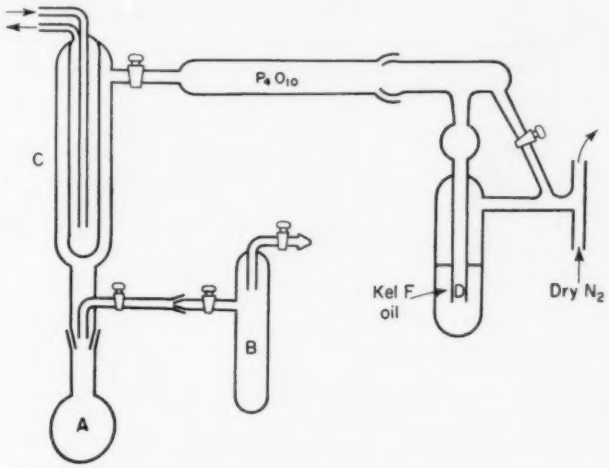

FIG. 1.

Reaction of lithium carbonate with dinitrogen tetroxide. Lithium carbonate was used as the starting material for the preparation of lithium nitrate. Liquid dinitrogen tetroxide reacts only very slowly with dry lithium carbonate, but the addition of a small amount of water speeds up the reaction. The reaction is practically complete after 96 hr of contact at temperatures between 0° and 20° yielding an essentially anhydrous product, even though up to 20 per cent water has been added. The overall equation, analogous to that suggested by ADDISON[1] for the sodium salt, seems to result from two successive reactions:

$$2N_2O_4 + H_2O \rightarrow 2HNO_3 + N_2O_3$$
$$2HNO_3 + Li_2CO_3 \rightarrow 2LiNO_3 + H_2O + CO_2$$
$$2N_2O_4 + Li_2CO_3 \rightarrow 2LiNO_3 + N_2O_3 + CO_2$$

The formation of N_2O_3 is evidenced by the appearance of a blue-green liquid at low temperatures. The experimental conditions and the yield of lithium nitrate obtained in different runs are summarized in Table 1. It should be noted that even where 19 per cent water is added, only trace amounts of nitrites are found in the product.

TABLE 1

Water content in carbonate	Reaction temperature (°C)	Reaction time (hr)	$LiNO_3$ (%)	$LiNO_2$ (%)
Dry at 140°C	17–21°C	38	26·35	—
Dry at 140°C	−5·0°C	33	30·13	—
Undried	0–10°C	36	43·30	—
1·5%* added	10–20°C	36	70·61	—
5·0%* added	10–20°C	48	81·3	0·1
15%* added	10–20°C	45	94·8	0·2
19%* added	0–20°C	96	98·2	0·2

* Based on dryweight of carbonate.

[1] C. C. ADDISON and J. LEWIS, JR., *J. Chem. Soc.* 1319–20 (1953).

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No evidence was found to indicate the formation of an adduct of lithium nitrate with dinitrogen tetroxide under the conditions of the experiment. We believe that the above experiments demonstrate a useful procedure for preparing anhydrous lithium nitrate.

Reactions of basic magnesium carbonate, magnesium oxide, and magnesium hydroxide with dinitrogen tetroxide. Reactions of liquid dinitrogen tetroxide with basic magnesium carbonate, magnesium oxide and magnesium hydroxide were carried out in accordance with procedures already described. The reactions take place much more slowly than in the case of the lithium compound and their rates appeared to decrease as the reaction proceeded. In no case was the reaction carried to completion. Typical experiments are summarized in Table 2.

TABLE 2

Reactant	Water† added (%)	Reactive temp. (°C)	Reaction time (hr)	$Mg(NO_3)_2$ in Product (%)
Basic magnesium carbonate	0	5–20	20	56·3
	0	0–20	54	68·2
Magnesium oxide	25	0–20	40	60·7*
	50	0–20	42	61·5*
Magnesium hydroxide	0	0–20	90	74*

* Based on the assumption that all the nitrogen present in the sample is in the form of NO_3^-, i.e. that there is no NO_2^- or N_2O_4 present.

† Based on the dry weight of carbonate, oxide, or hydroxide.

It is believed that the slowing down of the reaction results from the formation of a layer of magnesium nitrate over the surface of the carbonate, oxide or hydroxide particles.

Reaction of hydrated magnesium chloride and anhydrous magnesium chloride with dinitrogen tetroxide. It was readily shown that various hydrates of magnesium chloride are easily converted to the corresponding hydrated nitrates without appreciable change in the hydration of the magnesium ion.

$$[Mg(H_2O)n]Cl_2 + 2N_2O_4 \rightarrow [Mg(H_2O)n](NO_3)_2 + 2NOCl$$

However, the reaction of anhydrous magnesium chloride with liquid dinitrogen tetroxide appears quite promising as a method for preparing anhydrous magnesium nitrate. Reaction of anhydrous magnesium chloride with liquid dinitrogen tetroxide at 20° for a period of nine days yielded a product having the composition expressed by the formula $Mg(NO_3)_2 \cdot 0{\cdot}62N_2O_4$, plus about 2 per cent of unreacted magnesium chloride. This product was a white powder with a low vapour-pressure of dinitrogen tetroxide but lost weight only very slowly at 25° under vacuum. When the product was kept in contact with liquid dinitrogen tetroxide an additional day the composition changed to correspond to the formula $Mg(NO_3)_2 \cdot 0{\cdot}74N_2O_4$. It is probable that the product contains an adduct of N_2O_4 with $Mg(NO_3)_2$ and that it consists of a mixture of $Mg(NO_3)_2$ with that adduct (probably $Mg(NO_3)_2 \cdot N_2O_4$). The X-ray diffraction pattern contains lines characteristic of anhydrous magnesium nitrate plus additional unassigned lines. When this product was heated to constant weight at 110° under vacuum the resulting product gave the following analysis. (Found: Mg, 15·82; N, 17·80; Cl, 1·77. Calcd. for $Mg(NO_3)_2$: Mg, 16·40; N, 18·90%). The product thus consists of 94·23% $Mg(NO_3)_2$ and 2·37% $MgCl_2$ with the balance no larger in amount than the insoluble impurity present in the original magnesium chloride. The X-ray diffraction pattern of the product agrees perfectly with that reported by HUEBEL[2] for anhydrous magnesium nitrate.

Reaction of magnesium perchlorate with dinitrogen tetroxide. The product of the reaction of magnesium perchlorate with dinitrogen tetroxide has an elemental composition corresponding roughly to the formula $Mg(ClO_4)_2 \cdot 2N_2O_4$, as shown in Table 3. The product could also be formulated as the nitrosonium salt of a complex anion, $[NO]_2[Mg(ClO_4)_2(NO_3)_2]$, or as the mixture $Mg(NO_3)_2 + 2NOClO_4$, all of which have the same elemental composition.

The simple molecular addition compound can be ruled out as the major component, since the infrared spectrum shows two bands of medium intensity at 2300 and 2270 cm^{-1}, characteristic of the

[2] J. HUEBEL, *Bull. Soc. Chim.* 162 (1952).

NO^+ ion,[3] and also a strong band at 1383 cm^{-1} which belongs to the NO_3^- ion. On the other hand the X-ray diffraction pattern indicates that both magnesium nitrate and nitrosyl perchlorate are major constituents of this product. The over-all reaction thus appears to be as follows:

$$Mg(ClO_4)_2 + 2N_2O_4 \rightarrow Mg(NO_3)_2 + 2NOClO_4$$

The hydration of this mixture yields $Mg(ClO_4)_2 \cdot 6H_2O$, probably through the reaction of perchloric acid with the nitrate. The thermal decomposition of the solid mixture in vacuum failed to give pure magnesium nitrate, as expected, but seems to give a mixture of nitrate and perchlorate containing 9–11 per cent nitrogen.

TABLE 3

Reaction temperature (°C)	Reaction time (hr)	Mg (%)	N (%)	N/Mg
0–15	26	5·42	14·4	4·6/1
0–20	56	6·22	14·0	3·90/1
Calculated for $Mg(ClO_4)_2 \cdot 2N_2O_4$		5·97	13·75	4·0/1

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Reaction of aluminium chloride with dinitrogen tetroxide. A large excess of dinitrogen tetroxide was condensed over a sample of Merck reagent grade anhydrous aluminium chloride held at dry-ice temperature. As the temperature was allowed to rise, reaction began even before the dinitrogen tetroxide was completely melted, yielding a red liquid (NOCl). The solid took on a spongy appearance and after one to two days stirring a yellow, crystalline compound appeared. The reaction was continued at the boiling point of dinitrogen tetroxide (21°) for five days, the remaining liquid removed, after which the solid product contained no appreciable chloride. The product was then dried under vacuum at 25° and analyzed.

	N(%)	Al(%)	Cl(%)	Ratio N/Al
Found	21·20	10·90	0·01	3·75/1·0
Calc. for $Al(NO_3)_3$	19·73	12·66	—	3·0/1·0
Calc. for $Al(NO_3)_3 \cdot N_2O_4$	22·97	8·84	—	5·0/1·0

The analysis corresponds to the empirical formula $Al(NO_3)_3 \cdot 0{\cdot}38N_2O_4$. The infra-red spectrum of the product contained a band of medium intensity at 2260 cm^{-1}, characteristic of the NO^+ ion, the same band appearing in the spectrum of $NO[AlCl_4]$ at 2238 cm^{-1}.[4] Strong bands also appear in the region 1460–1600 cm^{-1}, characteristic of the nitrate group (—ONO_2) in covalent nitrates.[5] Two other bands at 1730 and 1275 cm^{-1}, can be attributed to either —ONO_2 or to N_2O_4.[3] Thus, we believe the reaction leads to a mixture of $Al(NO_3)_3$ and $NO[Al(NO_3)_4]$ in accordance with the equations:

$$AlCl_3 + 3N_2O_4 \rightarrow Al(NO_3)_3 + 3NOCl; \qquad Al(NO_3)_3 + N_2O_4 \rightarrow NO[Al(NO_3)_4]$$

When heated to 80° under vacuum for 4 hr, the yellow, crystalline solid loses 33 per cent of its weight and becomes white. Analysis of the white product:

	Al(%)	N(%)	Ratio N/Al
Found	15·5	17·18	2·13/1·0
Calc. for $Al(NO_3)_3$	12·66	19·73	3·0/1·0
Calc. for $Al_2O(NO_3)_4$	16·98	17·61	2·0/1·0

The infra-red spectrum of this product shows a much weaker NO^+ band than the above and two very strong —ONO_2 bands at 1570 and 1610 cm^{-1}. It appears, therefore, that most of the $NO[Al(NO_3)_4]$ has decomposed to $Al(NO_3)_3$, and that some of the $Al(NO_3)_3$ has been converted to a basic aluminium nitrate such as $Al_2O(NO_3)_4$ in accordance with the equation:

$$2Al(NO_3)_3 \rightarrow Al_2O(NO_3)_4 + 2NO_2 + \tfrac{1}{2}O_2$$

[3] C. C. ADDISON and B. J. HATHAWAY, *J. Chem. Soc.* 1468 (1960).
[4] O. J. MILLER and D. WATSON, *J. Chem. Soc.* 1369 (1957).
[5] C. C. ADDISON and B. M. GATEHOUSE, *J. Chem. Soc.* 613 (1960).

DISCUSSION

ADDISON and his co-workers have pointed out that dinitrogen tetroxide can act as a potential source of both NO_2^- and NO_3^- ions through the two dissociation mechanisms:

$$N_2O_4 \rightleftarrows NO_2^+ + NO_2^-$$

$$N_2O_4 \rightleftarrows NO^+ + NO_3^-$$

The results reported herein show that in its reactions at or near room temperature with lithium carbonate, with magnesium oxide, carbonate, chloride and perchlorate, and with aluminium chloride, dinitrogen tetroxide reacts in accordance with the second of these possibilities. Previously reported work with sodium carbonate and sodium hydroxide, with calcium carbonate,[6] with zinc carbonate and zinc sulphide,[7] and with sodium peroxide, calcium oxide, and zinc,[8] are in agreement with this result:

It has previously been shown[9–12] that zinc nitrate, copper nitrate, and ferric nitrate form dinitrogen tetroxide adducts which have in some instances been formulated as nitrosyl salts containing nitrato metalate complexes, as e.g. $(NO)_2[Zn(NO_3)_4]$ for $Zn(NO_3)_2 \cdot 2N_2O_4$. This study, however, presents the first reported evidence for the formation of a dinitrogen tetroxide adduct of aluminium nitrate and additional evidence[13] for an adduct of magnesium nitrate. Furthermore, the evidence obtained indicates, that since these magnesium nitrate and aluminium nitrates adducts have only a low vapour-pressure of oxides of nitrogen at room temperature, the bonding of the dinitrogen tetroxide to the metal nitrate is moderately strong.

Finally we believe that the preparation of anhydrous magnesium nitrate by the thermal decomposition of the reaction product of anhydrous magnesium chloride and dinitrogen tetroxide is a distinctly more convenient method than the currently used procedure involving the reaction of magnesium hydroxide with dinitrogen pentoxide.

It is interesting to note that even in the presence of excess dinitrogen tetroxide, the hydration of the magnesium ion is unaffected and the reaction of hydrated magnesium chloride with dinitrogen tetroxide affects only the chloride ion.

The failure to obtain pure anhydrous aluminium nitrate from the thermal decomposition *in vacuo* of the product of the reaction of dinitrogen tetroxide with anhydrous aluminium chloride, and the formation instead of a basic aluminium nitrate is not entirely unexpected in view of the known reaction of boron trichloride with dinitrogen tetroxide[14] to yield boric oxide and nitrosyl chloride. It is possible that the decomposition of the aluminium nitrate-dinitrogen tetroxide adduct under somewhat less stringent conditions than those used in this study might yield pure, anhydrous aluminium nitrate.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 135 to 137. Pergamon Press Ltd.

URANYL BROMIDES OBTAINED FROM AQUEOUS SOLUTION

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(*Received* 28 *March* 1960; *in revised form* 12 *August* 1960)

Abstract—Uranyl bromide can be crystallized from acid solution as the very hygroscopic trihydrate. Part of the water can be removed at 60°C without decomposition, but irreversible decomposition takes place at 115°C. Its saturated solution is 6·5 M, viscous, very dark red and of density 3·36 g/ml. Recrystallization from ether or isopropanol yields organic solvate-hydrates. The basic bromide, $UO_2(OH)Br{\cdot}2H_2O$, has been crystallized from acid-deficient uranyl bromide solutions. It forms stable dilute aqueous solutions, but its concentrated solutions deposit hydrated uranium trioxide.

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NEARLY all the work on uranyl bromides prepared from solution is quite old and has been summarized by KATZ and RABINOWITCH[1]. Anhydrous uranyl bromide can be obtained[2] by the oxidation of uranium tetrabromide at 160°C or by the bromination of uranium dioxide at 265°C. SHCHUKAREV and co-workers[3] have prepared the hydrated bromide from water-vapour and the anhydrous bromide and from solution by evaporation in a desiccator over sulphuric acid. The basic bromide has not been previously reported, although the analogous basic chloride has been observed[4] in a study of solubility in the system UO_3–HCl–H_2O and in earlier work. In this investigation the hydrated bromide and a new basic bromide were obtained from solution, and some of their properties were observed.

EXPERIMENTAL

Temperature-dependent observations, such as densities and solubilities, were made without mechanical thermostatting, but at a laboratory temperature which remained in the range 26–27°C.

Analyses were performed by groups of the Analytical Chemistry Division under the supervision of G. R. WILSON and W. R. LAING. Bromide was determined by a Volhard procedure, uranium by a potentiometric titration with ferric sulphate, water by the Karl Fischer method, hydroxide by acidimetry after precipitation of uranium with ferrocyanide, and carbon by combustion. X-ray diffraction characterizations and identifications were by R. L. SHERMAN of the Analytical Chemistry Division.

Preparation of $UO_2Br_2{\cdot}3H_2O$

Solutions of uranyl bromide are readily prepared by dissolving uranium trioxide in hydrobromic acid. These solutions must be concentrated by evaporation before crystallization can take place. An unmeasured excess of acid was used to decrease the solubility of the bromide and to compensate for loss of acidity during evaporation, which could lead to formation of the basic bromide. After the solution was concentrated to a thick, deep-red, nearly opaque syrup, crystals formed on cooling. However, if evaporation was carried out until the solution approached the composition of the solid, the solid bromide formed a cement-like cake hard to remove from the vessel without redissolution. After crystallization, the uranyl bromide was separated from the bulk of the liquid on a coarse sintered glass filter connected to the building vacuum system. The remaining water and excess

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[2] J. PRIGENT, *C.R. Acad. Sci., Paris* **247**, 1737 (1958).
[3] S. A. SHCHUKAREV, I. V. VASIL'KOVA, V. M. PROZDOVA and K. E. FRANTSEVA, *Russ. J. Inorg. Chem.* (English Translation) **4**, 15 (1959).
[4] C. A. KRAUS, Manhattan District Report A-360 (1942).

hydrobromic acid were evaporated by stoppering the top of the filter and continuing the vacuum for from several hours to three days. Washing the solution from the crystals was impossible since uranyl bromide is soluble in water-miscible liquids. The crystals varied in colour from yellow-orange to red-orange; traces of occluded intensely coloured solution probably masked the true yellow colour. The yellow colour typical of uranyl salts has been observed on rehydration of bromide samples dried and partly decomposed by heating at 175°C. The bromide could be stored in glass-stoppered vessels in a desiccator; on exposure to air it rapidly deliquesced. It did not evolve hydrogen bromide on standing at room temperature, as claimed[1] in the early work. The density of the hydrated bromide, determined by benzene displacement, was 4·32 g/ml. (Found: U, 49·3, 49·2, 48·8; Br, 32·9, 33·6, 32·5; H_2O, 11·51, 10·48, 10·62. Calc. for $UO_2Br_2 \cdot 3H_2O$; U, 49·2; Br, 33·0; H_2O, 11·2%).

Solubility of $UO_2Br_2 \cdot 3H_2O$

A small volume of water was added to uranyl bromide hydrate, and after dissolution successive portions of solid were added until undissolved solid remained on standing overnight. Over a four-day period portions of the solution were withdrawn into a 500 μl pipette, weighed, and analyzed for uranium and for bromide ion. The averages and average deviations found were uranium, 6·51 ± 0·06 M; bromide, 13·0 ± 0·1 M; density, 3·36 ± 0·01 g/ml; no trend with time was observable.

Crystallization of uranyl bromide from organic solvents

Uranyl bromide is known[1] to be soluble in organic oxygen compounds and to form addition compounds with some of them. Attempts to crystallize uranyl bromide, by vacuum evaporation at room temperature of solutions of the hydrate in ethyl ether and in isopropyl alcohol, yielded yellow-orange crystals containing both water and organic solvent. Attempted evaporation of the organic solutions by heating resulted in reduction of uranium to a black insoluble powder.

Thermal decomposition of hydrated uranyl bromide

The weight changes of several samples of $UO_2Br_2 \cdot 3H_2O$ were observed for different periods of heating. Loss of about one-third of the water was achieved at 60 C without decomposition. Partial decomposition to various yellow solids resulted at 125–175 C. At 200–350 C, the decomposition product was brick red, amorphous to X-rays, and identified as nearly pure uranium trioxide by its ease of solution in hydrochloric acid and the only very slight turbidity resulting from adding silver nitrate to its solution in nitric acid. The weight loss on decomposition corresponded to the formation of $UO_3 \cdot H_2O$ at 200 C and UO_3 at 350 C. It is notable that a brick-red form of uranium dioxide has been claimed[1] as a decomposition product of the anhydrous bromide.

Preparation of basic uranyl bromide

The basic uranyl bromide was first observed during attempts to crystallize the normal bromide from aqueous solution. Observations made during this investigation indicate that the basic bromide is the saturating solid at room temperature for solutions ranging in bromide/uranium ratio from 1·1 to near 2; this is very similar to the behaviour reported by KRAUS[4] for the analogous chloride. If equimolar quantities of uranium trioxide and hydrobromic acid are combined, the solid precipitating is the hydrated oxide and not the basic bromide.

When uranium trioxide was dissolved in hot uranyl bromide solution and crystallization allowed to take place, the solid phases included the basic bromide. The bromide/uranium ratio was kept well above the room-temperature limit of 1·1 to avoid precipitation of the oxide during cooling. The solids were collected on a sintered-glass filter and washed with isopropanol or ethyl ether to remove normal bromide. The fine yellow needles obtained were stable to the atmosphere, not visibly soluble in ethyl ether, isopropanol, or an ethyl ether solution of uranyl bromide. The density, determined by benzene displacement, was 4·95 g/ml. The X-ray diffraction pattern is given in Table 1. (Found: U, 58·7; Br, 19·8; H_2O, 13·24; OH^-, 2·33 meq/g: Calc. for $UO_2(OH)Br \cdot 2H_2O$: U, 59·1; Br, 19·8; H_2O, 13·4 (the OH^- ion responds to the analysis as a water molecule); OH^-, 2·48 meq/g).

Interaction of the basic bromide with water

Basic uranyl bromide dissolved readily when mixed rapidly with sufficient water to give dilute solutions. These solutions were more intensely coloured than unhydrolyzed uranyl solutions of the same concentration. Solutions as concentrated as 0·1 M lost part of their uranium as precipitated

hydrated oxide on standing several days. Solutions as dilute as 0·01 M appeared stable indefinitely. Concentration by evaporation of a stable basic bromide solution led to oxide deposition. Treatment of basic bromide with insufficient water to consume the sample gave a solution 2·73 M in U(VI), 3·0 M in bromide, and of density 1·87 g/ml. The yellow residue contained two components, unreacted basic bromide which could be dissolved in a large volume of water, and an insoluble material identified by X-ray diffraction as $UO_3 \cdot 2H_2O$. Thus the above composition is the solution simultaneously saturated with oxide and basic bromide. The saturating oxide need not be the dihydrate, since hydration may have occurred during the washing to remove from the basic bromide.

TABLE 1.—X-RAY DIFFRACTION PATTERNS OF BASIC URANYL BROMIDES

$UO_2(OH)Br \cdot 2H_2O$				$UO_2(OH)Br$			
Intensity*	d(Å)	Intensity	d(Å)	Intensity	d(Å)	Intensity	d(Å)
w	8·9	*vvw*	2·22	*m*	8·0	*w*	2·40
>*w*	5·4	*vvw*	2·12	*m*	7·45	*vvw*	2·34
>*w*	5·15	*w*	2·09	*w*	6·4	*vw*	2·23
vvw	4·9	*w*	2·05	*vvw*	5·4	*w*	2·18
s	4·4	*vw*	2·01	<*m*	4·75	*vw*	2·10
vvw	4·1	*vw*	1·98	*vvw*	4·45	*w*	2·05
m	3·85	*vw*	1·94	<*m*	4·05	*w*	1·98
>*w*	3·65	*vw*	1·90	*s*	3·79	*w*	1·94
vvw	3·05	*vw*	1·865	*w*	3·70	*w*	1·89
vw	3·0	*w*	1·83	*w*	3·55	*vw*	1·86
vw	2·94	*w*	1·81	*w*	3·28	*vvw*	1·76
<*w*	2·88	*w*	1·77	*vvw*	3·18	*vvw*	1·72
m	2·75	*w*	1·75	*w*	3·08	*vw*	1·705
vvw	2·69	*vvw*	1·72	*w*	2·98	*vvw*	1·68
vvw	2·64	*w*	1·66	>*w*	2·90	*vvw*	1·58
vvw	2·56	*vw*	1·62	*w*	2·82	*vvw*	1·53
w	2·52	*w*	1·57	*w*	2·68	*vvw*	1·51
w	2·47	*vvw*	1·53	*w*	2·58	*vvw*	1·445
vw	2·44	*vw*	1·51	*w*	2·54	*vw*	1·40
>*w*	2·37	*vw*	1·48				
vw	2·32	*w*	1·35				

* *s*—strong, *m*—medium, *w*—weak, *v*—very.

Thermal dehydration of the basic bromide

The basic bromide, $UO_2(OH)Br \cdot 2H_2O$, was heated overnight at 105°C with no change in appearance or weight. Heating three days at 115°C resulted in a weight loss of 8·10 per cent, and another day at 200°C produced a total loss of 9·15 per cent, corresponding to 2·03 moles of water per mole of basic bromide. The resulting "anhydrous basic bromide" showed a different X-ray diffraction pattern (Table 1) from the hydrated basic bromide and from previously known compounds. Dissolution in water gave a solution similar to that obtained from the hydrated basic bromide. (Found: U, 63·5; Br, 21·3; OH^-, 2 meq/g. Calc. for $UO_2(OH)Br$: U, 64·9; Br, 21·8; OH^-, 2·7 meq/g).

CONCLUSIONS

Uranyl bromide has been crystallized from acidic aqueous solutions. It was shown by analysis to be the trihydrate, in agreement with SHCHUKAREV[3] and in disagreement with early investigators[1] who claimed $UO_2Br_2 \cdot 7H_2O$. The previously unreported basic bromide has been obtained from acid-deficient uranyl bromide solutions as the dihydrate, $UO_2(OH)Br \cdot 2H_2O$. This compound can be dehydrated to $UO_2(OH)Br$ at 200°C. It is decomposed by water to uranium trioxide and a solution containing more bromine atoms than uranium atoms.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 138 to 145. Pergamon Press Ltd.

ALKALINE OXIDATION OF AMERICIUM; PREPARATION AND REACTIONS OF Am(IV) HYDROXIDE*

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(*Received* 20 *June* 1960)

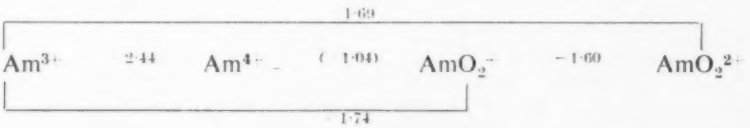
Abstract—A pink slurry of $Am(OH)_3$ is converted quantitatively into the black hydroxide (or hydrous oxide) of tetravalent americium by hypochlorite oxidation in dilute base. Preparation of tetravalent americium from aqueous solution has not been previously reported. This material dissolves in nitric or perchloric acid and disproportionates according to the equation: $2Am(IV) = Am(V) + Am(III)$. It dissolves in sulphuric acid giving Am(VI) and Am(III), with a minimum of half of the Am(V) produced from the simple disproportionation of Am(IV) being consumed by a consecutive reaction:

$$Am(IV) + Am(V) = Am(VI) + Am(III).$$

Revision from $+0{\cdot}4$ to at least $-0{\cdot}5$ V is suggested for the value of the standard potential of the $Am(OH)_3$, $Am(OH)_4$ couple.

Oxidation of $Am(OH)_3$ past $Am(OH)_4$ is observed with both ozone and peroxydisulphate. Details are given for a new and convenient method for producing AmO_2^{2+} in dilute acid solution based on the ozone oxidation of $Am(OH)_3$. Ozone oxidizes $Am(OH)_3$ in 0·1 M NaOH to a soluble yellow complex of Am(VI).

THE aqueous oxidation states of americium include Am(III), Am(V) and Am(VI), but there is a significant vacancy; i.e., the lack of Am(IV).[1-7] Americium in the tetravalent state is known only in three compounds, AmO_2[8], AmF_4 and $KAmF_5$[9], which are prepared under anhydrous conditions. Pertinent to this fact are the potentials in aqueous acid solution[7,10,11] relating Am^{3+}, AmO_2^+ and AmO_2^{2+}, and including estimates for the hypothetical Am^{4+}.



* This work was sponsored by the U.S. Atomic Energy Commission.

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Using these potentials as a basis for prediction, it is clear that Am^{4+} should be highly unstable in acid with respect to disproportionation into Am^{3+} and AmO_2^+. The reaction of Am^{4+} with AmO_2^+ to produce AmO_2^{2+} and Am^{3+} is predicted in molar acid. The reduction of Am(IV) to Am(III) by water is also energetically favourable.

In contrast to this, the situation in alkaline solution is much more favourable for stabilization of tetravalent americium. LATIMER[12] outlined in detail the basis for his estimate of the $Am(OH)_3$, $Am(OH)_4$ couple in molar base and gave +0·4 V, which also has been listed in recent texts[13,14]. This value is apparently in error both in sign and magnitude and we are unable to obtain it on recomputation. For reasons which are developed later, we suggest −0·5 V as the value for the $Am(OH)_3$, $Am(OH)_4$ couple.

From a preparative chemist's point of view, it is very interesting that this potential is nearly 2 V more positive than the Am^{3+}, Am^{4+} potential in acid solution, and should lie well within the range of chemical oxidizing agents. Two common oxidizing agents whose potentials in molar base exceed this value are hypochlorite and ozone:[15]

$$ClO^- + H_2O + 2e^- = Cl^- + 2OH^-;\ E_B^\circ = +0{\cdot}89\ V$$

$$O_3 + H_2O + 2e^- = O_2 + 2OH^-;\ E_B^\circ = +1{\cdot}24\ V.$$

Tetravalent americium had not hitherto been prepared from aqueous solution and it was primarily to attempt its preparation that the present work was begun.

EXPERIMENTAL AND DISCUSSION

Oxidation of $Am(OH)_3$ *to* $Am(OH)_4$ *with hypochlorite*

Interestingly, hypochlorite oxidation was tried perhaps fifteen years ago in the early days of americium chemistry by CUNNINGHAM[16]. He reported a single experiment on a microgram scale in which $Am(OH)_3$ was precipitated by excess base containing ClO^- and a darkening of the precipitate was observed. We find that a light pink slurry of $Am(OH)_3$ turns brown-black when heated with NaOCl in the presence of NaOH. Presence of additional alkali is apparently necessary, since either 0·6 M NaOCl or 0·2 M NaOCl by itself produced less than 10 per cent oxidation to $Am(OH)_4$. With 0·2 M NaOH present, variation of NaOCl from 0·2 to 0·6 M seemed to produce $Am(OH)_4$ equally well.

In a typical experiment, 5 mg of freshly precipitated $Am(OH)_3$ was stirred with 2·5 ml of 0·2 M NaOCl–0·2 M NaOH in a boiling water-bath for 30 min. The dark precipitate which formed was centrifuged and heated again for 30 min with a second portion of 0·2 M NaOCl–0·2 M NaOH. The precipitate was centrifuged and washed twice in 2 ml portions of 0·001 M NaOH with warming to promote coagulation. After centrifugation, the material was then ready for subsequent experiments.

Oxidation of $Am(OH)_3$ *using peroxydisulphate*

Treatment of 5 mg of $Am(OH)_3$ in 0·1 M NaOH with excess solid $K_2S_2O_8$ for 2 hr in a boiling water bath yielded an olive-tan precipitate. Under these conditions, the average oxidation number of the americium was 4·53, showing that oxidation *past* $Am(OH)_4$ had occurred.

However, $Am(OH)_4$ could be prepared using peroxydisulphate in very strong base. Americium was added to hot, 7 M potassium hydroxide saturated in potassium peroxydisulphate and the resulting

[12] W. M. LATIMER, *Oxidation Potentials* (2nd Ed.) Chap. 21. Prentice-Hall, New York (1952).
[13] Ref. 4, p. 129.
[14] Ref. 5, p. 357.
[15] Ref. 12, Table 85.
[16] B. B. CUNNINGHAM, *The Transuranium Elements*, (Edited by G. T. SEABORG and J. J. KATZ) NNES, Plutonium Project Record, Div. IV, Vol. 14B, pp. 1363–1369. McGraw-Hill, New York (1949).

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slurry was kept at 90° for 1 hr. The final precipitate was then washed carefully to remove excess reagent. The average oxidation number in the hydroxide was 4·0 ± 0·1. Since the hypochlorite oxidation produces $Am(OH)_4$ so conveniently, the variation in products of the peroxydisulphate oxidation was not investigated further.

Disproportionation of Am(IV) *in* H_2SO_4

As mentioned in connection with the americium potential diagram, Am^{4+} would be expected to undergo the following reactions in acid:

(1) simple disproportionation; $2Am(IV) = Am(V) + Am(III)$

(2) redox reaction; $Am(IV) + Am(V) = Am(VI) + Am(III)$.

There is some interesting work by ZAITSEV *et al.*[3,17] in which AmO_2 (obtained by ignition of americium oxalate) was dissolved in H_2SO_4. With 1 M H_2SO_4 they found

TABLE 1.—DISSOLUTION OF $Am(OH)_4$ IN H_2SO_4

H_2SO_4 (M)	Temp (°C)	Valence states after dissolution (%)			Av. oxidation number in final solution*
		III	V	VI	
2	25	64·6	9·8	25·6	3·96
2	25	60·2	11·5	28·3	4·08
1	25	67·6	5·4	27·0	3·92
1	25	65·3	4·8	29·8	3·99
1	0	67·1	3·5	29·4	3·95
0·1	25	58·4	24·7	16·9	4·00
0·1	25	57·9	23·4	18·7	4·03
0·05	25	63·5	14·1	22·4	3·95

* Final solution was 0·003–0·012 M in total americium.

Am(III) and Am(VI) in solution in proportions practically equivalent to the sum of reactions (1) and (2); i.e., $3Am(IV) = Am(VI) + 2Am(III)$. They did not work in other acids and thus were not able to isolate reaction (1).

Dissolution of our black hydroxide (prepared by hypochlorite oxidation) in sulphuric acid was also found to give Am(VI) and Am(III) with some Am(V). The concentrations of americium(III), (V) and (VI) were determined spectrophotometrically, using the Cary Recording Spectrophotometer, Model 14 M. In each experiment, the average oxidation number was found to be four within the accuracy of our spectrophotometric determinations. The results are shown in Table 1.

Since the average oxidation number remains four, it follows that Am(IV) must *not* have been reduced by water, and the observed products can be fully accounted for by reactions (1) and (2). This may be somewhat unexpected since the rapid reduction of Am(IV) by water is often postulated. Appreciable reduction of Am(IV) by water is found on dissolution of AmO_2. ZAITSEV *et al.*[17] found that the reduction of Am(IV) by water is of increasing importance when AmO_2 is dissolved in > 1 M H_2SO_4; e.g., 27 per cent reduction in 2 M H_2SO_4, and 64 per cent in 6 M H_2SO_4. The

[17] A. A. ZAITSEV, V. N. KOSYAKOV, A. G. RYKOV, YU. P. SOBOLEV and G. N. YAKOVLEV, Institute of Atomic Energy, Academy of Sciences, Moscow, U.S.S.R. (1960); (NP–7518).

reduction of Am(IV) by water was also involved in the thermochemical work on the Am^{3+}, Am^{4+} potential.[11]

The data in Table 1 also show that variation in H_2SO_4 concentration changes the amount of reaction (2) significantly but do not allow the effects of hydrogen ion and sulphate (or bisulphate) ion to be separated. Therefore, we determined the effect of

TABLE 2.—EFFECT OF SULPHATE CONCENTRATION ON REACTION (2) AT CONSTANT (H^+)

H^+ (M)	HSO_4^- (M)	SO_4^{2-} (M)	Am(VI)(%) (equals % Reaction 2)
0·095*	0	0	3·2
0·095	0·049	0·051	19·2
0·094	0·37	0·38	27·3

* Ionic strength was kept at 2·0. Li_2SO_4, $LiClO_4$ and $HClO_4$ were used.

sulphate at constant hydrogen ion. Table 2 shows these results. Since, from the stoichiometry, the Am(VI) produced cannot exceed one-third of the Am(IV) initially present, the approach to this figure shows that sulphate clearly promotes Am(IV) reacting with Am(V); i.e., reaction (2). Particularly noteworthy is the fact that in the absence of sulphate (i.e., in $HClO_4$) reaction (2) is almost completely suppressed.

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Disproportionation of Am(IV) *in* HNO_3 *and* $HClO_4$

Observation of Am(IV) disproportionation in acids having weaker complexing anions than sulphate was desired. An additional series of experiments was performed

TABLE 3.—DISSOLUTION OF $Am(OH)_4$ IN HNO_3

HNO_3 (M)	Temp (°C)	Valence states after dissolution (%)			Av. oxidation number in final solution*
		III	V	VI	
2	0	55·4	40·4	4·2	3·93
1	60	52·2	44·5	3·3	3·99
1	25	50·9	46·1	3·0	4·01
1	25	52·3	43·5	4·2	4·00
1	0	55·1	41·0	3·9	3·94
0·1	0	52·6	47·4	0·0	3·95
0·05	0	55·0	45·0	0·0	3·90

* Final solution was 0·005–0·008 M in total americium.

in which $Am(OH)_4$ was dissolved in various concentrations of nitric acid. Just as in the case of perchloric acid (see line 1, Table 2), only a few per cent reaction (2) was observed. Results are tabulated in Table 3.

In one case, an approximation to a minimum value for the rate of disproportionation of Am(IV) in 0·05 M HNO_3 at 0° could be made by noting the rate of change of the Am(III) and Am(V) absorption maxima. Under these conditions, and assuming a reaction second order in Am(IV), we estimate k_1 in the equation

$$-d[\text{Am(IV)}]/dt = k_1[\text{Am(IV)}]^2$$

to be $> 3{\cdot}7 \times 10^4$ l. mole^{-1} hr^{-1}. In acidities $> 0{\cdot}1$ M, dissolution of the $Am(OH)_4$ is too rapid to permit observation.

Proof of oxidation number in $Am(OH)_4$

(1) As can be seen from Tables 1 and 3, the average oxidation number in the solutions obtained by dissolution of the black hydroxide in acid was *four*. Although this information was noted with jubilation, one had to rule out that the black hydroxide was not just a fortuitous mixture of Am(III) and Am(V).

TABLE 4.—DISSOLUTION OF $Am(OH)_4$ IN THE PRESENCE OF Am(V)

Media	% Reaction (2), no added Am(V)	% Reaction (2), with added Am(V)
0·1 M HNO_3	0	4·5
0·1 M H_2SO_4	18·2	28·7
0·5 M H_2SO_4	—	54·5
1·0 M H_2SO_4	27·4	44·0

(2) The contrasting reactions of the black hydroxide on dissolution in HNO_3 and in H_2SO_4 provide convincing evidence that it is the hydroxide (or hydrous oxide) of tetravalent americium. Since Am(III), Am(V) and Am(VI) do not react with each other under the conditions of these experiments, the products obtained in the different acids can be fully accounted for only by assuming that all of the americium was originally in its tetravalent state.

(3) Tetravalency of americium in the new compound was also confirmed when the black hydroxide was dissolved in an acidic solution of Am(V). Decrease of the Am(V) concentration could only occur through oxidation by Am(IV). It was found that reaction (2) is still essentially negligible even when $Am(OH)_4$ is dissolved in HNO_3 containing an amount of Am(V) roughly equal to the amount of $Am(OH)_4$. As expected, reaction (2) is significantly increased in sulphuric acid when additional Am(V) is present. As a separate experiment, it was confirmed that the concentration of Am(V) in 0·5 M sulphuric acid is *not* changed when $Am(OH)_3$ is dissolved in it. Results are shown in Table 4.

(4) We had hoped that absorption lines characteristic of a new valence state would be observed. However, the absorption spectrum of the brown-black slurry gave only general absorption from 4500 to 10,000 Å with the Cary Recording Spectrophotometer. In contrast, the absorption spectrum of an $Am(OH)_3$ slurry gives sharp lines only slightly shifted from their characteristic positions in acid solution. The absorption spectra data thus rule out the presence of $Am(OH)_3$ in the black material even though no significant absorption from Am(IV) was found.

In very dilute HNO_3; e.g., 0·05 M, particularly at 0°C, $Am(OH)_4$ dissolves tantalizingly slowly and it was possible to examine this process in the spectrophotometer. A high general absorption was observed which diminished as the characteristic absorption peaks of Am(III) and Am(V) grew in. However, no discrete absorption lines were found which could be attributed to Am(IV).

Attempted dissolution of $Am(OH)_4$ *in complexing media*

Attempts were made to effect solution of $Am(OH)_4$ in various complexing media.

In acid solution, success would depend on the ability of a ligand to lower the activity of Am(IV) thus depressing the competing reaction of disproportionation. In basic media, the ligand must compete with the remarkable insolubility (K_{sp} ca. 10^{-56}) of $Am(OH)_4$.[12] Americium tetrahydroxide was prepared by hypochlorite oxidation and was slurried with various complexing agents with the results shown in Table 5.

TABLE 5.—BEHAVIOUR OF $Am(OH)_4$ IN VARIOUS COMPLEXING MEDIA

Reagent	Results
2 M Li_2SO_4 at pH 10	No dissolution, slow reduction to Am(III) only
2 M Li_2SO_4 at pH 10 + 0·1 M EDTA*	No dissolution, slow reduction to Am(III) only
0·2 M DTPA† at pH 10	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing
0·2 M DTPA at pH 6	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing
0·2 M DTPA at pH 4	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing
0·2 M DTPA at pH 2	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing
Glacial acetic acid	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing
Glacial acetic acid + 0·001 M DTPA	Only broad general continuum from 10,000–4,000 Å with Am(III) maxima slowly increasing
Dibutyl phosphoric acid	Continuum as above, with Am(III) slowly increasing; roughly 10% of Am appeared as Am(VI)

* EDTA = ethylenediaminetetraacetic acid
† DTPA = diethylenetriaminepentaacetic acid

At pH 10 (even in DTPA), the black Am(IV) hydroxide precipitate appeared quite stable and the growth of Am(III) noted here is probably due only to slow reduction of the Am(IV) caused by the ^{241}Am α-radiation. From the Th(IV)–DTPA constant,[18] one might predict the Am(IV)–DTPA complexity constant as ca. 10^{28}. Evidently, this is not sufficient to stabilize Am(IV). Dissolution in (undiluted) dibutyl phosphoric acid resulted in some Am(VI), presumably as a result of disproportionation of Am(IV) in this medium.

[18] R. F. BOGUCKI and A. E. MARTELL, *J. Amer. Chem. Soc.* **80**, 4170 (1958).

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Oxidation of $Am(OH)_3$ *with ozone*

Ozone is one of the most powerful alkaline oxidizing agents, $E_B^\circ = -1{\cdot}24$ V. Its potential exceeds the value of not only the $Am(OH)_3$, $Am(OH)_4$ couple which we estimate at ca. −0·5 V, but exceeds the $Am(OH)_4$, AmO_2OH (−0·7 V) and the AmO_2OH, $AmO_2(OH)_2$ (−1·1 V) couples.[12] Oxidation of $Am(OH)_3$ at least to AmO_2OH and possibly to $AmO_2(OH)_2$ is thus expected with ozone.

We find that ozone oxidizes $Am(OH)_3$ *past* $Am(OH)_4$ at all pH's from neutrality to 1 M NaOH. In 1 M NaOH, oxidation is very slow, requiring work at 0°C to increase the ozone solubility. Oxidation in 0·1 M NaOH at 25°C causes considerable oxidation to Am(VI), forming a soluble yellow complex.

Oxidation of a slurry of $Am(OH)_3$ in water with ozone occurs readily and was developed for the routine preparation of Am(VI) from Am(III). The following technique is recommended. Ozone is passed through a slurry of $Am(OH)_3$ in water at 90° for 1–2 hr, allowing the incoming ozone to stir the slurry vigorously. Dilute acid is then added dropwise to dissolve *part* of the oxidized material. The pH should not drop below 5 during this operation. If the slurry is made *too* acid (~0·1 M H^+) at this time, any Am(III) (formed either from unoxidized $Am(OH)_3$ or from disproportionation of Am(IV)) cannot be oxidized further. Ozonization is continued for another hour. Additional acid is then slowly added to dissolve the remainder of the slurry and treatment with ozone is continued to oxidize any Am(V) to Am(VI).

Ozone oxidation of $Am(OH)_3$ *to a hydroxy complex of* Am(VI)

Evidence was obtained for the formation of a soluble hydroxide species of Am(VI). When $Am(OH)_3$ in 0·1 M NaOH was treated with O_3, the supernatant liquid was yellow and contained considerable americium. The amount of soluble americium increased with time of ozonization. Spectral examination of this yellow solution indicated a continuum from 10,000 to 4,000 Å with no discernible maxima. After this yellow solution was slowly made acidic while being treated with ozone, the solution showed only the characteristic spectrum of hexavalent americium.

An attempt was made to produce this yellow hydroxide complex starting with an acidic solution of Am(VI). The experiment is complicated by the observation that, while AmO_2^{2+} is stable in acid solution at least up to pH 3, partial reduction to Am(V) occurs around neutrality. Therefore, ozone was bubbled through the Am(VI) solution while 2 M NaOH was added dropwise. A dark-brown precipitate formed at about pH 7 which *redissolved* to give a yellow solution at pH 13. The spectrum of this yellow solution was identical with that obtained previously.

When an acid solution containing Am(V) is made basic, a colourless supernatant is obtained although Am(V) is slightly soluble in base. Treatment with ozone produces the yellow colour of the hexavalent americium hydroxide complex. The spectrum of the hydroxide complex of Am(VI) was unaltered by addition of NaF or Na_2SO_4. These anions affect considerably the colour of Am(VI) in acidic media.

Remarks on the $Am(OH)_3$, $Am(OH)_4$ *potential*

LATIMER[12] estimated K_{sp} for $Am(OH)_4$ as 10^{-56} based on the progression in hydroxide solubility products of Th(IV), U(IV), and Pu(IV). He estimated K_{sp} of $Am(OH)_3$ as $2{\cdot}7 \times 10^{-20}$. The Am^{3+}, Am^{4+} couple was taken as −2·18 V. For 1 M hydroxide, one estimates −0·02 V for the $Am(OH)_3$, $Am(OH)_4$ couple, not +0·4 V

as given. Allowing for the latest value of the Am^{3+}, Am^{4+} couple (−2·44 V)[11] gives ca. −0·3 V for the $Am(OH)_3$, $Am(OH)_4$ couple in molar base. Several arguments suggest that this value is not sufficiently negative:

(1) Our experience at pH 7–8 is that K_{sp} of $Am(OH)_3$ is about 10^{-24}. This would make the $Am(OH)_3$, $Am(OH)_4$ potential more negative by ca. −0·24 V.

(2) Oxygen does not oxidize $Am(OH)_3$, although oxidation might be anticipated if the $Am(OH)_3$, $Am(OH)_4$ couple were less negative than the oxygen couple, $E_B^\circ = -0{\cdot}4$ V.

(3) Alkaline permanganate oxidizes $Am(OH)_3$ forming both manganate and MnO_2 as reduction products. The MnO_4^{2-}, MnO_4^- value of −0·56 V or the MnO_2, MnO_4^{2-} value of −0·6 V may be controlling, although this is an insignificant difference for our purposes. (It might be mentioned here that bromate produced no oxidation of $Am(OH)_3$ although the bromide, bromate couple is −0·6 V in molar base. However, bromate is a notoriously slow oxidizing agent except in acid.)

We thus conclude that the $Am(OH)_3$, $Am(OH)_4$ potential in molar base is at least as negative as −0·5 V.

Since hypochlorite, $E_B^\circ = 0{\cdot}89$ V, apparently does not oxidize $Am(OH)_3$ past $Am(OH)_4$, even after long treatment, LATIMER's estimate for the $Am(OH)_4$, AmO_2OH couple (−0·7 V) should perhaps be made more negative by a few tenths of a volt also.

Note added in proof—We are indebted to Prof. B. B. Cunningham, Univ. of Calif., Berkeley, for the following observation which he sent after reading a draft of our paper:

The published estimate of the value of the $Am^{+3} = Am^{+4} + e^-$ potential[11], was based on the assumption that the observed heat of reaction of AmO_2 with 6M HNO_3 − 0.1 M HBF_4 was due to the heat of solution of the dioxide plus the heat of reduction of Am(IV) by water. At the time this experimental work was done it was not known that the V and VI states of americum could be produced by dissolution of Am(IV) in acid solution.

It has since been found that in the solvent used in the calorimeter runs considerable amounts of Am(V) and Am(VI) are formed. Since the heats of formation of Am(V) and Am(VI) have been determined[10], the old estimate of the potential of the $Am^{+3} = Am^{+4} + e^-$ couple may be corrected for disproportionation. The corrected value is about −2.6 to −2.9 V. However, this must be regarded as tentative until more extensive data are obtained.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 146 to 151. Pergamon Press Ltd.

TUNGSTATE COMPLEXES WITH CATECHOL

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(*Received* 24 *May* 1960; *in revised form* 17 *August* 1960)

Abstract—Tungstate ion complexes with catechol to form anions containing tungstate and catechol in the ratios 1:1, 1:2 and 1:3; the compositions of the anions in solution have been obtained by Job's method and by conductometric and potentiometric titrations. On precipitation with heavy metal cations, the 1:1 complex is usually obtained, but the 1:2 complex is the most stable species in solution. The change from the 1:2 to the 1:1 complex can be followed by pH measurement. Possible structures of the complex anions are discussed.

THE solid complexes of tungstates with catechol have been known for some time.[1,2] The nature of these complexes is doubtful, although it has been suggested that either water molecules or hydroxyl ions are eliminated, leaving the tungstate ion with an oxygen co-ordination number of four as in the simple tungstate ion, or six as in the polytungstates. For example, the complexes of catechol and tungstate isolated by FERNANDES[1] and by WEINLAND[2] *et al.* were given the formulae

$$NH_4H[WO_3.C_6H_4O_2(H_2O)]$$
$$NH_4H[WO_2(C_6H_4O_2)_2]H_2O$$
$$(C_6H_5N)_2[WO_2(C_6H_4O_2)_2]C_6H_4(OH)_2.4H_2O$$

These formulae indicate a tungsten co-ordination number of six and suggest the breaking of a tungsten–oxygen bond. The latter suggestion seems unlikely, because of the ease with which the reaction can be reversed in solution. Little is known of the chemistry of these complexes in solution apart from the identification by HALMEKOSKI[3] of the 1:2 complex. The aim of the present investigation was to identify the various species present in solution and to relate them, if possible, to the precipitates obtained.

EXPERIMENTAL AND RESULTS

When equimolar solutions of sodium tungstate and catechol are mixed, a yellow colour develops immediately. If the solution is made strongly alkaline, the colour is first intensified and then turns brown, due to oxidation of the catechol. If the original solution is acidified to pH ~3 a deep red colour develops, followed by the slow precipitation of a mixture of tungstic acid and a tungstic acid catecholate; the composition of this precipitate varies according to the concentration of the solution used and the rate of acidification.

Three methods were used to determine the composition of the complexes present in solution, viz. JOB's method of continuous variations,[4] conductometric titration and potentiometric titration. Solutions of sodium tungstate and catechol when mixed absorb light strongly in the range 400–500 mμ. The Job plot at 400 mμ obtained in the usual manner is recorded in Fig. 1*A*. The solutions were left in a thermostat at 20°C for 30 min before recording the spectra. If, however, the spectra were taken immediately on mixing, a slightly different Job plot was obtained (Fig. 1*B*). These graphs show that

[1] L. FERNANDES, *Gazzetta*, **55**, 424 (1925).
[2] R. WEINLAND, A. BABEL K. GROSS, and H. MAI, *Z. Anorg. Chem.* **150**, 177 (1926).
[3] J. HALMEKOSKI, *Ann. Acad. Sci. Fenn.* A **11**, 96
[4] P. JOB, *Ann. Chim.* **11**, 6, 97 (1936).

the predominant species present was the 1:2 complex, with a 1:1 complex probably being formed first. The rather prolonged shoulder on the Job plot in curve A suggests that a 1:3 complex might also be formed. A small correction, varying between 3 and 7 per cent of the optical density, had to be made to the light absorption readings to allow for the increased absorption with increasing pH between 5 and 9. This correction was calculated from the absorption of a series of standard solutions at different pH values. The alternative method of using buffered solutions was rejected because of the possibility of the tungstate ion complexing with some of the buffer ions. The decrease in absorption with pH is probably due to the competing tendency for the tungstate ion to polymerise in acid solution.

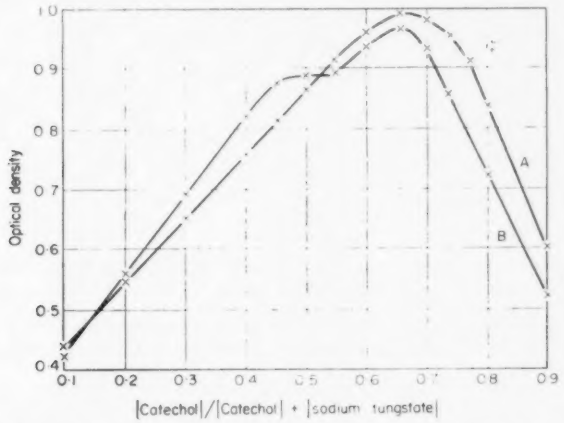

FIG. 1.—Graph *A*—Job's plot at 400 mμ. using tungstate-catechol solutions held at 20° C for 30 min.
Graph *B*—Job's plot at 400 mμ. for spectra recorded immediately after mixing.

Although there were probably at least three complexes present in solution, the 1:2 complex appeared to be the most stable. To obtain an approximate equilibrium constant for the reaction

$$WO_4^{2-} + 2C_6H_4(OH)_2 \rightleftharpoons WO_4[C_6H_4(OH)_2]_2^{2}$$

the following method was applied. The 1:2 complex was assumed to be the main coloured component of the system, and Beer's Law was assumed to apply; the concentration of the complex will then be proportional to the absorption at a fixed wavelength. It is also assumed that complexing is complete when a large excess of the ligand is used. The absorption of more dilute solutions, where chelation is incomplete, was then found, and by substitution, values of K were calculated. Using excess catechol to establish the absorption at complete chelation, K was found to be $5{\cdot}2 \times 10^6$. This value can only apply to solutions which have a tungstate concentration of approximately 10^{-3} M, since when progressive amounts of sodium tungstate are added to a fixed concentration of catechol, the absorption passes through a maximum and then decreases (Fig. 2); this suggests that even in alkaline solution with increasing pH between 8 and 9, the tungstate ion tends to polymerise with increasing concentration. This agrees with the results of SADDINGTON and ANDERSON[5], who showed by diffusion experiments that the degree of aggregation of tungstate ions below pH 9 depended on the concentration of tungstate ions as well as of hydrogen ions. Thus a solution of sodium tungstate in water probably produces simple hydrated tungstate ions only in very dilute solution.

[5] K. SADDINGTON and J. S. ANDERSON, *J. Chem. Soc.* **5**, 381 (1949).

The existence of the 1:2 complex was confirmed by potentiometric titration. The buffer zone obtained when sodium tungstate was titrated with hydrochloric acid could be limited by adding catechol to the tungstate solution. When the ratio of tungstate to catechol in the solution was 1:2, the buffer zone was eliminated (Fig. 3).

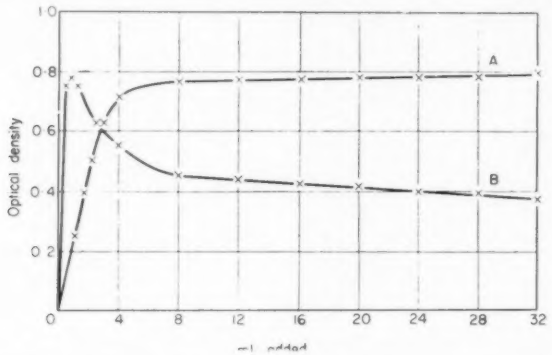

FIG. 2.—Graph *A*—Addition of excess $2{\cdot}2 \times 10^{-3}$ M catechol to a fixed concentration of sodium tungstate (2 ml of a 2×10^{-3} M solution diluted to 50 ml with catechol solution plus water).
Graph *B*—Addition of excess $2{\cdot}0 \times 10^{-3}$ M sodium tungstate to a fixed concentration of catechol (2ml of a $2{\cdot}2 \times 10^{-3}$ M solution diluted to 50 ml with tungstate solution plus water).

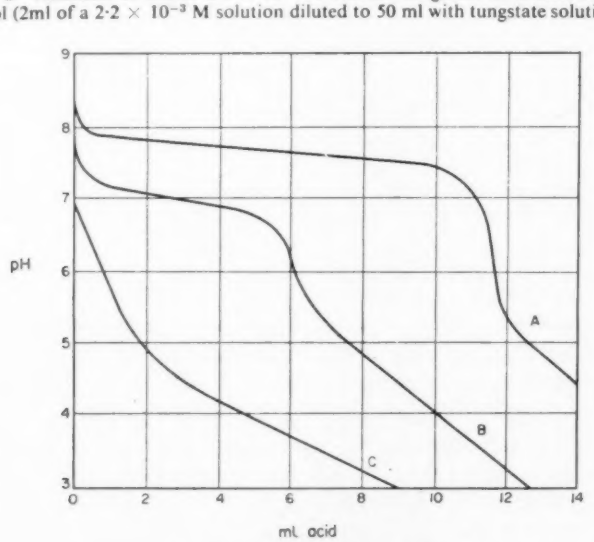

FIG. 3.—Potentiometric titrations
Graph *A*—0·1 N hydrochloric acid added to 10 ml 0·1 M sodium tungstate solution.
Graph *B*—0·1 N hydrochloric acid added to 10 ml of a solution 0·1 M in sodium tungstate and 0·1 M in catechol.
Graph *C*—0·1N hydrochloric acid added to 10 ml of a solution 0·1M in sodium tungstate and 0.2 M in catechol.

The Job experiments described above indicate a stepwise addition of catechol to the tungstate ion. To confirm this catechol was added slowly to a sodium tungstate solution and the conductance of the solution was measured after each addition. The results obtained are shown in Fig. 4. The stoicheiometric ratio of the stable 1:2 complex is shown. However, there is also a slight but definite break when 1 ml of catechol is added, indicating a probable stepwise addition of catechol. A conductometric titration was also carried out of a solution of sodium tungstate containing excess catechol with

hydrochloric acid. This showed an inflexion after one equivalent of acid had been added (Fig. 5). Thus it appears that the complex ion in solution is the salt of either a weak monobasic acid or of a polybasic acid (probably dibasic) having one weakly acidic hydrogen ion. The latter seems to be the correct interpretation, because after the addition of one equivalent of hydrogen ion the coloured ion migrates to the anode on electrolysis. This view also agrees with the isolation of the acid salts described previously.[1]

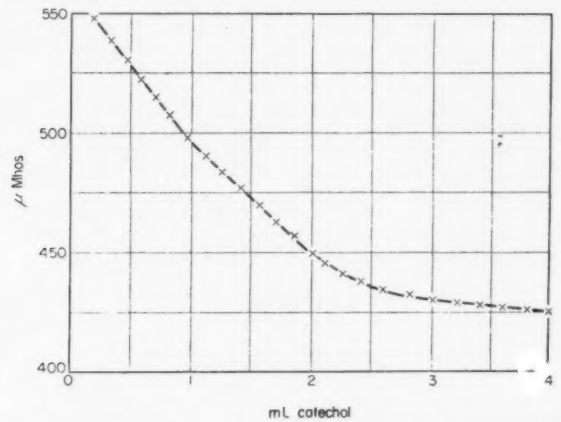

FIG. 4.—Conductometric titration of a 1×10^{-3} M sodium tungstate solution with a 0·1 M catechol solution.

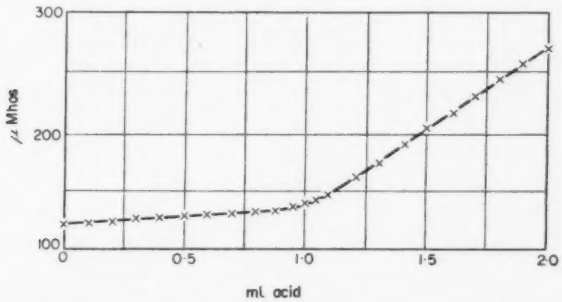

FIG. 5.—Conductometric titration of a solution 1×10^{-3} M in sodium tungstate and 5×10^{-3} M in catechol with 0·1 N hydrochloric acid.

When a solution of sodium tungstate is added to a solution of catechol which is adjusted to the same pH with dilute sodium hydroxide, the pH of the mixed solution rises. This could be due to the liberation of hydroxyl ions from the tungstate ions or from the catechol, or to removal of hydrogen ions which are incorporated into the complex, from solution If these postulates are correct, the number of hydrogen ions absorbed or of hydroxyl ions liberated would be similar to the concentration of the complex, provided that excess catechol were used. This however, was not the case. When 25 ml of a $3{\cdot}15 \times 10^{-2}$ M sodium tungstate solution were diluted to 50 ml with a 1·0 M catechol solution of the same pH, the pH rose from 8·00 to 8·20, corresponding to the removal of approximately 4×10^{-9} g. equivts. of hydrogen ion. The change in hydrogen ion concentration was thus very much smaller than the concentration of the complex (which was approximately equal to that of the initial tungstate solution).

Similarly, the change in concentration of hydroxyl ion, 6×10^{-7} g. equivts., was also very much smaller. The other possibility is that the equilibrium

$$C_6H_4(OH)_2 \rightleftharpoons C_6H_4(OH)O^- + H^+, K = 3{\cdot}56 \times 10^{-10}$$ [6]

is disturbed. Assuming that all the tungstate was complexed to form the 1:2 complex, the calculated change in pH corresponding to the change in concentration of catechol agreed with the measured change in pH. Thus the change in pH appears to be due to the decrease in concentration of the un-ionised catechol, which therefore must be the complexing ligand.

Previous work,[1,2] as mentioned above, describes the preparation and properties of salts of the 1:1, 1:2 and 1:3 complexes. All the salts prepared were divalent, with the 1:1 and 1:2 complexes also giving acid salts. Although the experiments described above indicate that the 1:2 complex is the most stable in solution, attempts to precipitate this complex with metallic cations which generally give insoluble tungstate precipitates resulted in the isolation of the 1:1 complex. For example, the addition of lead nitrate to solutions containing sodium tungstate and catechol in the proportions 1:1, 1:2, 1:3, 1:4, 1:10 resulted in the precipitation of red solids which all gave on analysis the formula $PbO.WO_3.C_6H_4(OH)_2$. (Found PbO, 39·8, WO_3, 40·6, $C_6H_4(OH)_2$, 19·2 from carbon analysis). (Calc. PbO, 39·5, WO_3, 41·0, $C_6H_4(CH)_2$, 19·5%). Salts of the 1:2 and 1:3 complexes were only obtained by using as precipitants organic cations such as guanidine or ammonia. The displacement of the second catechol molecule from the 1:2 complex on precipitating the 1:1 complex with barium could be followed by the change in pH of the solution. When a solution of barium chloride was added to a solution 0·1 M in sodium tungstate and 1·0 M in catechol, both solutions being at pH 8, and the resulting solution left for 30 mins before filtering, the pH of the filtrate was 6·0. This difference in pH agrees with that expected if one molecule of catechol is liberated for each molecule of the complex which is precipitated.

The infra-red spectra of the anhydrous lead and barium salts were compared with that of catechol in the region of the —OH bands at 3350 and 3450 cm^{-1}. If the bonding were due to elimination of water of or hydroxyl ion to give a W—O—C link the OH bands would be expected to disappear. This was not found. Some broadening of the band at 3350 cm^{-1} was observed, as would be expected with increased hydrogen bonding.

DISCUSSION

The pH changes on mixing sodium tungstate and catechol solutions and on precipitating the 1:1 complex with barium chloride, suggest that the complexing agent is the catechol molecule itself, giving a divalent complex ion in each case. The anions of the 1:1 and 1:2 complexes appear, from analytical and conductometric results, to possess one weakly-acidic hydrogen ion. The bonding might be through the donation of a pair of electrons from the oxygen atoms in the hydroxyl groups to the tungsten atom, giving an oxygen co-ordination number of six for the tungsten atom in the 1:1 complex as in most solid tungstates. The O—O distance in catechol is 2·60 Å, while in the distorted WO_6 octahedra in heteropoly acids, the O—O distance varies from 2·60 to 3·10 Å[7]; structurally, the oxygen atoms of catechol could fit into the WO_6

[6] H. PAULY, K. SCHUBEL and K. LOCKEMANN, *Ann.* **383,** 307 (1911).
[7] J. F. KEGGIN, *Proc. Roy. Soc.* A **144,** 75 (1934).

octahedra without distortion of the carbon-oxygen bond. There are no recorded structures for oxygen-bonded eight co-ordinated tungsten atoms, but in the $Mo(CN)_8^{4-}$ ion the carbon to carbon distances have been calculated to lie in the range 2·50–3·18 Å.[8] The catechol oxygen atoms could fit into a structure of this type without much deformation in the case of the 1:2 complex.

Acknowledgement—The author wishes to thank Mr. T. C. BROWN for his help in some of this work.

[8] J. L. HOARD and H. H. NORDSIECK, *J. Amer. Chem. Soc.* **61**, 2853 (1939).

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J. Inorg. Nucl. Chem. 1961, Vol. 17, pp. 152 to 158. Pergamon Press Ltd

THE STRUCTURE OF CHROMIUM AZIDE: ITS INSTABILITY CONSTANT IN AQUEOUS SOLUTIONS

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(*Received* 4 *August* 1960)

Abstract—A spectrophotometric study of chromium(III) azide solutions has shown that the intense green colour formed from the violet chromium(III) nitrate and sodium azide in dilute solutions, is due to a mono-azido-chromium(III) complex with two absorbancy maxima at wavelengths 442 and 605 mμ. The slope ratio method was applied and suggested the presence of such a complex. The results were confirmed by the continuous variation method. The molar ratio method was also applied for the determination of the instability constant of the 1:1 complex. It was found to be $(2{\cdot}14 \pm 0{\cdot}136) \times 10^{-2}$. There is a tendency for a stepwise formation of azide-rich complexes upon gradual increases in azide concentration. A deep blue solution, with absorbancy maxima at wavelengths 480 and 650 mμ, was formed in solutions containing a large excess of azide. Migration experiments proved the existence of positively and negatively charged complex ions in the green and the deep blue solutions respectively.

EARLIER investigators[1] mentioned that chromium azide could be formed from chromium salts and sodium azide. They claimed that the aqueous solutions of chromium azide undergoes hydrolysis by heating. The behaviour of these solutions towards the action of ammonium hydroxide and silver nitrate solutions respectively is similar to that of $Cr[(H_2O)_4Cl_2]Cl.H_2O$ towards the same reagents. In 1922, solid chromium azide was separated[2] by the evaporation of a solution prepared by mixing dry crystalline chromium(III) nitrate in absolute alcohol with excess of sodium azide. A dark green hygroscopic mass was isolated. Basic chromium azide, $Cr(N_3)_2OH$ or $CrN_3(OH)_2$, was obtained if any moisture was present. The sodium salt of hexa-azido-chromium(III) acid $H_3Cr(N_3)_6$ was also separated by adding excess sodium azide to a concentrated solution of chromium hydroxide in hydrazoic acid. In a study of the exchange reactions between chromium (III) ions and complex ions[3], the mono-azido-chromium (III) ion CrN_3^{2+} was prepared by the reaction of chromium (II) and ferric azide complexes in dilute perchloric acid solution about 0·3 M in azide ion.

The analogy between metal azides in general and the corresponding thiocyanates led to the investigation of the structure and the determination of the dissociation constants of the azides of many transitional metal ions such as Fe(III)[4], Co(II)[5], Cu(II)[6], and the uranyl ions[7]. It is well known that the octahedral hexa-aquo-chromium(III) ion, $Cr(H_2O)_6^{3+}$, is violet but aqueous solutions of chromic salts are often green as a result of replacement of water molecules in the complex by the anions

[1] E. OLIVERI-MANDALA, *Gazz. Chim. Ital.* **49**, 43 (1919); *Chem. Abstr.* **14**, 701 (1920).
[2] E. OLIVERI-MANDALA and G. COMELLA, *Gazz. Chim. Ital.* **52**, 112 (1922); *Chem. Abstr.* **16**, 2089 (1922).
[3] L. D. BALL and L. E. KING, *J. Amer. Chem. Soc.* **80**, 1091 (1958).
[4] H. K. EL-SHAMY and F. G. SHERIF, *Egypt. J. Chem.* **1**, 35 (1958); **1**, 257 (1958); **2**, 217 (1959).
[5] P. SENISE, *J. Amer. Chem. Soc.* **81**, 4196 (1959).
[6] G. SAINI and G. OSTOCALI, *J. Inorg. Nucl. Chem.* **8**, 346 (1958).
[7] H. I. FEINSTEIN *Analyt. Chim. Acta.* **15**, 288 (1956).

present. It is therefore expected that chromium(III), like any other transitional metal ion, would form azide complexes. Work in this line is being carried out in this laboratory. Solutions containing the violet form of the chromium(III) ion and the azide ion have been investigated using the spectrophotometer. The formula for the mono-azido-chromium complex CrN_3^{2+} has been confirmed and its instability constant determined in dilute solutions. Some information regarding the nature of the complex ions in solutions containing high concentration of azide ion is also presented.

EXPERIMENTAL

The hydrated violet form of chromium nitrate was used. A stock solution, about 0·2 M, was prepared and analysed gravimetrically as the oxide and checked volumetrically by oxidation to dichromate, addition of excess of a standard ferrous solution and titration of the excess Fe^{2+} with dichromate. Other more dilute solutions were prepared by diluting the stock solution.

A stock solution of sodium azide, about 1 M, was prepared and analysed volumetrically for the azide by direct titration against standard silver nitrate solution using potassium chromate as an indicator.[8] More dilute solutions were prepared by diluting the stock solution and always checked for the azide content before use.

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To carry out optical measurements, the various solutions were prepared by mixing the required amounts of the stock solutions and making up to 25 ml. The azide solutions were always added to the chromium solutions slowly and with continuous stirring, to avoid turbidity, especially in solutions containing excess azide. The green chromium azide solutions were always kept in the dark for 2 hr before measurements. This time was found to be sufficient to maintain colour stability. The colour intensities were measured by means of a Unicam Quartz Spectrophotometer, model S.P.500. Two glass cells, 1 cm thickness each, were used, one for the test solution and the other for the blank. The blank used was a solution containing the same concentration of chromium nitrate as that present in the test solution. When concentrated solutions of chromium azide were too dark to permit measurements in these cells, glass plungers of 0·9 cm thickness were dipped in, giving a light path of 0·1 cm.

A sodium perchlorate solution, 1 M, was prepared and analysed gravimetrically as potassium perchlorate. This solution was used to adjust the ionic strength in some experiments. It was also used as a medium for the migration experiments. These were carried out in a tube of a shape similar to the letter *W*, and of 1 cm diameter. A separating funnel was attached to the centre of this tube. The test solutions were introduced through two capillaries leading to the inside arms of the *W* tube.

RESULTS

Absorption spectrum of the chromium azide solution

A solution that was 0·02 M with respect to chromium and to azide ions was deep green in colour. The absorbancies were measured over a wavelength range of 400–700 mμ. Two absorbancy maxima were found, one at 442 mμ and the other at 605 mμ. When a 0·02 M chromium(III) nitrate solution was measured against a water blank, two maxima were found at 410 mμ and 570 mμ respectively.

In one set of experiments the chromium(III) concentration was kept constant at 0·006 M and the azide ion concentration was varied from 0·006 to 0·120 M. The absorbancies of the different solutions were measured over the same range of wavelength. In solutions with molar ratios of chromium to azide from 1:1 to 1:6, the absorbancy maxima were the same, showing that at such dilutions the formation of more than one coloured complex was difficult. However, shifts in the maxima towards longer wavelengths were apparent when higher concentrations of azide ion were added to the chromium solutions. The possibility of the stepwise formation of azide-rich

[8] A. MAJRICH, *Chem. Obsor.* **5**, 3 (1930); *Chem. Abstr.* **24**, 4480 (1930).

complexes might be anticipated. The results of these measurements are depicted in Fig. 1. In another set of experiments the azide ion concentration was kept constant at 0·128 M and the chromium ion concentration was varied from 0·004 to 0·020 M. The absorption curves were measured over the same wavelength range. No shift in the maximum absorptions were found out. These observations are in agreement with the assumption that the formation of the azide-rich complexes depends wholly upon the

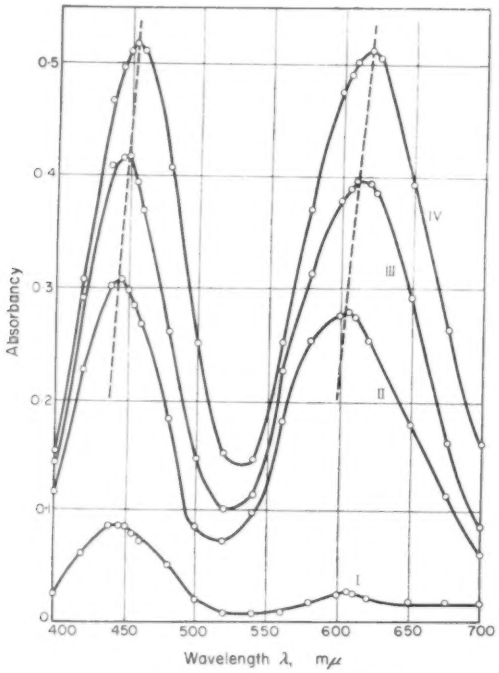

FIG. 1.—Variation in the absorbancy of chromium(III) azide (Cr^{3+} = 0·006 M) with increasing concentration of azide ion. N_3^- (I) 0·006 M; (II) 0·036 M; (III) 0·060 M; (IV) 0·120 M.

azide ion concentration, but is independent of the chromium ion concentration as long as the azide is the component in excess.

Structure of the chromium azide complex

The slope ratio method devised by HARVEY and MANNING[9] was applied for the determination of the structural formula of the green coloured species in dilute solutions of chromium and azide. Two sets of experiments were carried out. In the first, the metallic ion concentration was kept constant and always in excess and the concentration of the ligand was varied. In the other, the concentration of the ligand was kept constant and also in excess and the concentration of the metallic ion varied. The absorbancies of the two sets of solutions were measured at the wavelength corresponding to the maximum absorption of the coloured species sought. Plots of the absorbancy values against the concentration of the variable should give straight

[9] A. E. HARVEY and D. L. MANNING, *J. Amer. Chem. Soc.* **72**, 4488 (1950).

lines. The ratio of the slopes of the two lines would be the same if the ratio of the two components forming the complex ion is 1:1.

The azide ion concentration was kept constant in one series of solutions at 0·008 M while the concentration of the chromium(III) varied from 0·00133 to 0·00400 M. In the second series, the chromium ion concentration was kept constant at 0·008 M and the azide ion varied from 0·00133 to 0·00400 M. The ionic strength of the two series of solutions was adjusted to a constant value of 0·052 by adding the required amounts

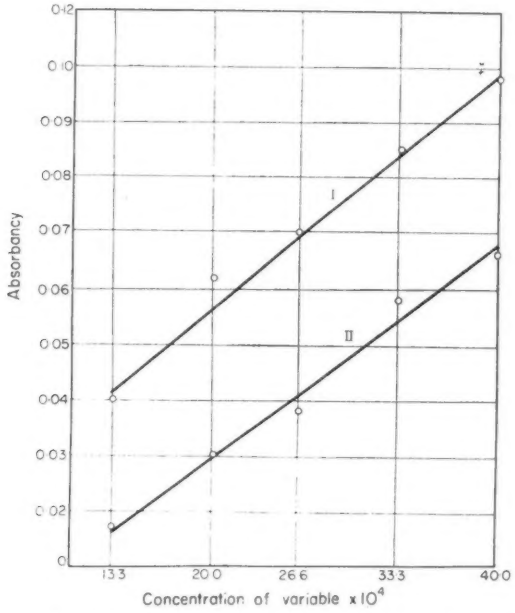

FIG. 2.—Absorbancies of chromium azide solutions at 440 mμ. (I) N_3^- concentration constant at 0·008 M and chromium(III) varied; (II) Cr^{3+} concentration constant at 0·008 M and azide varied. The ionic strength was kept constant at 0·052.

of 1 M sodium perchlorate solution. The absorbancies were measured at the wavelength 440 mμ. The results are shown in Fig. 2. The ratio of slope I of slope II of the two straight lines was found to be 1·05:1 respectively. This would not occur unless the formula of the coloured species is CrN_3^{2+}.

The continuous variation method of JOB[10] was applied by mixing equimolecular solutions of chromium(III) and azide in different ratios. The total concentration was kept constant at 0·008 M in one series of solutions. The ionic strength was also kept constant at 0·044 by addition of sodium perchlorate solution. Absorbancy measurements were obtained at the wavelengths 440 and 480 mμ. A free choice of wavelengths was permissible as the absorption curves in Fig. 1 do not intercept, according to the rules of GOULD and VOSBURGH[11]. The results are shown in Fig. 3. An inspection of the curves indicates that maximum intensities lie at a mole fraction of azide of 0·5, which provides strong evidence for the formation of a complex having the ratio 1:1 of

[10] P. JOB, *C.R. Acad. Sci., Paris* **180**, 928 (1925).
[11] R. K. GOULD and W. C. VOSBURGH, *J. Amer. Chem. Soc.* **64**, 1630 (1942).

chromium to azide. However, the curves being unsymmetrical, and broadened on the side of high azide concentration, may also indicate the existence of complexes rich in azide. Further investigations on the application of JOB's method to solutions of chromium(III) and azide of higher concentrations in aqueous and in aqueous-non-aqueous mixtures are being carried out in our laboratory. The results will be reported later.

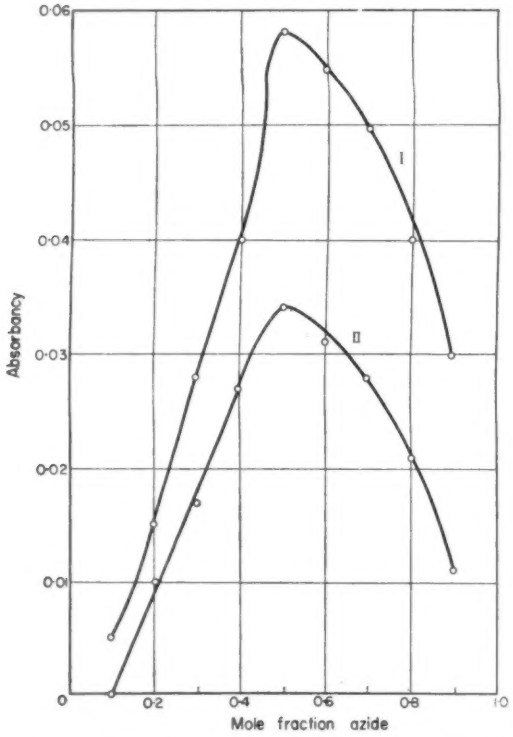

FIG. 3.—Continuous variation method; total concentration of chromium(III) and azide ions is 0·008 M. The ionic strength was kept constant at 0·044. (I) Wavelength 440 mμ; (II) Wavelength 480 mμ.

Degree of ionization and instability constant

The molar ratio method proposed by YOE and JONES[12] was applied for the investigation of the equilibrium

$$[CrN_3^{2+}] = Cr^{3+} + N_3^- \tag{1}$$

$$x = a - x + b - x \tag{2}$$

where a is the molar concentration of Chromium(III), b that of azide. x is the degree of ionization and is known in terms of absorbancy at a given wavelength. The instability constant K for the dissociation reaction can be given by the expression

$$K = \frac{(a - x)(b - x)}{x} \tag{3}$$

[12] J. H. YOE and A. L. JONES, *Industr. Engng. Chem.* Analyt. Ed. **16**, 111 (1944).

If the concentration of a is kept constant, that of b is varied, and the absorbancy of the resultant coloured solution is plotted against the variable, a smooth curve will be obtained that runs in a linear form for a certain b, then its slope decreases gradually until it becomes zero. This will be true if the complex formed has a significant dissociation, assuming Beer's law is obeyed. In the presence of a large excess of b, the colour will reach its saturation value with a constant absorbancy C, where almost all

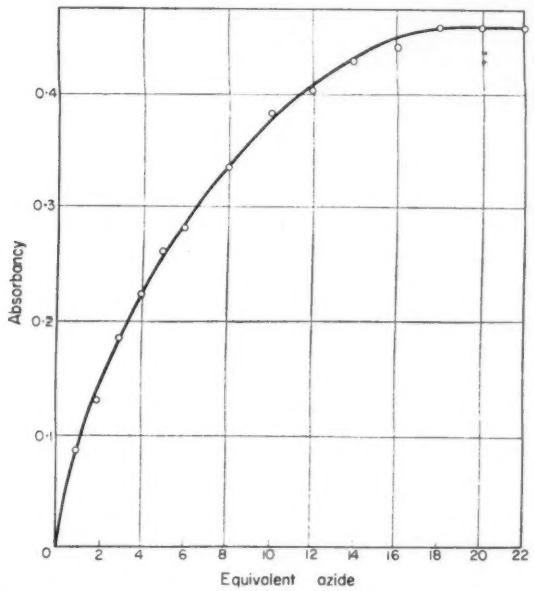

FIG. 4.—Absorbancies of chromium(III) azide solutions (Cr^{3+} = 0·006 M) as a function of increasing azide ion concentration. (N_3^- = 0–0·132 M) at wavelength 440 mμ.

the chromium(III) ions present are included on the left-hand side of equation (1). At this point the absorbancy C will be proportional to a. Any absorbancy c for any value of b less than that leading to saturation would be proportional to the degree of ionization x. Thus

$$\frac{x}{c} = \frac{a}{C} \tag{4}$$

Knowing x, a and b, the value of K can be calculated.

In one series of fourteen solutions the concentration of a was kept constant at 0·006 M, that of b varied from 0·006 to 0·0132 M. Measurements were taken at the wavelength 440 mμ. When the absorption values of the green solutions were plotted against the azide equivalents, the curve in Fig. 4 was obtained. The gradual and smooth increase in the intensity of the green colour indicated that the complex formed was undergoing an appreciable dissociation. The values of the instability constant K was calculated and found to be constant in solutions having a ratio of 1:1–1:6, chromium (III) to azide respectively. The mean value for K was $2{\cdot}14 \pm 0{\cdot}096 \times 10^{-2}$. In solutions containing higher equivalents of the azide, K was found to decrease slowly. This is in conformity with the previous observation that only one coloured species was

being formed in solutions containing not more than six equivalents of azide per one of chromium(III) at these dilutions, while other azide-rich complexes might form in presence of higher ratios of azide, Fig. 1. The results are given in Table I. The calculated values for the instability constant K', assuming that the di-azido-chromium complex $Cr(N_3)_2^+$ was formed, were not constant.

Higher complexes of chromium azide

When a large excess of 1 M solution of sodium azide was added to 0·1 M violet solution of chromium(III) nitrate, a green colour was first formed, then the solution

TABLE 1.—INSTABILITY CONSTANTS OF CHROMIUM AZIDE SOLUTIONS

$Cr^{3+}:N_3^-$	Mole fraction Cr^{3+}	$K \times 10^3$	$K' \times 10^5$
1:1	0·50	2·29	2·1
1:2	0·33	2·20	88
1:3	0·25	2·27	141
1:4	0·20	2·15	188
1:5	0·167	1·96	208
1:6	0·143	1·98	255
1:7	0·125	1·59	240
1:8	0·111	1·34	232
1:10	0·090	1·03	250

became turbid, and eventually a greenish white precipitate was formed. However, by leaving this mixture overnight, the precipitate, which was presumably chromium basic azide, redissolved in the excess azide producing a deep blue coloured solution. The absorption curve of this solution was measured over a wavelength range of 400–800 mμ. Two maxima were found, the first at 480 mμ and the second at 650 mμ. Studies on the nature and the stability of this blue complex are in progress.

Migration experiments

The *W* tube was filled with 1 M sodium perchlorate solution. A green chromium azide solution, 0·006 M, containing equal amounts of chromium(III) and azide was introduced carefully into the centre of the tube. The diffusion of the boundaries was avoided by using this high concentration of the perchlorate solution. A potential gradient of 1 Vt/cm was applied to the ends of the tube. The green boundary migrated towards the cathode. This indicates the existence of the positively charged ion CrN_3^{2+} in solution. Another chromium azide solution was prepared, with a concentration of 0·02 M with respect to Cr^{3+} and 0·8 M with respect to N_3^- ions. This solution was kept overnight to let the precipitate formed redissolve. The final solution was deep blue in colour. This solution was introduced in the *W* tube and the same current was applied. The blue boundary was found to migrate towards the anode. This indicates the presence of a negatively charged complex ion, rich in azide.

J. Inorg. and Nucl. Chem., 1961, Vol. 17, pp. 159 to 167. Pergamon Press Ltd.

EVIDENCE FOR THE EXISTENCE OF THE PERMANGANYL ION IN SULPHURIC ACID SOLUTIONS OF POTASSIUM PERMANGANATE

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(*Received* 19 *May* 1960; *in revised form* 26 *July* 1960)

Abstract—The green solution produced when potassium permanganate is dissolved in concentrated sulphuric acid has been investigated. The results of cryoscopic and conductance studies of this solution can be explained on the basis of the equation $KMnO_4 + 3H_2SO_4 \rightarrow K^+ + H_3O^+ + MnO_3^+ + 3HSO_4^-$.

The visible and ultra-violet spectrum of the solution can be shown to be consistent with the presence of a planar MnO_3^+ ion of symmetry D_{3h}.

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IT has long been known that dissolution of a small amount of potassium permanganate in concentrated sulphuric acid (specific gravity 1·82 or higher) yields a clear sage green solution.[1]

The addition of large amounts of potassium permanganate or the cautious addition of small amounts of water to the green solution leads to the precipitation of manganese heptoxide, a very unstable oil which appears red by transmitted light and metallic green by reflected light.[1,2] The nature of the green solution seems to have escaped serious investigation. FRANKE[2a] suggested that the green colour was due to the presence of $(MnO_3)_2SO_4$; he however had no experimental evidence for the existence of this compound and based his suggestion solely on the dubious analogy to the known compound MnO_3F, which is a green gas. This suggestion seems to have been accepted uncritically by later authors.[3]

This paper reports the results of an investigation undertaken to elucidate the composition of this green solution.

EXPERIMENTAL

Materials. Reagent grade 97 per cent sulphuric and reagent grade oleum were mixed to give acid of the desired concentration which in most cases was about 99·95 per cent acid as determined by the freezing point. The potassium permanganate and all other chemicals used were of C.P. grade and used as received.

Cryoscopic measurements. The cryoscopic determinations were made in a modified Beckmann type apparatus. The cell was of all glass construction and so designed that the solute could be added and the solution stirred vigorously without exposing the contents of the cell to the atmosphere. The cell was tight enough so that the freezing point of a sample of sulphuric acid underwent no significant change in one week's time.

Because of the instability of the solutions and the great tendency of the solutions to supercool,

[1a] H. ASCHOFF, *J. Prakt. Chem.* (1) **81**, 29 (1860), [b]H. ASCHOFF, *Chem. News* **6**, 57 (1861).
[2a] B. FRANKE, *J. Prakt. Chem.* (2) **36**, 31 (1887); [b] E. THORPE and F. HAMBLY, *J. Chem. Soc.* **53**, 182 (1888); [c]J. LOVEN, *Ber. Dtsch. Chem. Ges.* **25**, Ref. 620 (1982); [d] F. R. LANKSHEAR, *Z. Anorg. Chem.* **82**, 97 (1913); [e] A. AIMON and F. FEHER, *Z. Elektrochem.* **38**, 137 (1932); [f] O. GLEMSER and H SCHRØDER, *Z. Anorg. Chem.* **271**, 293 (1953).
[3] W. LATIMER and J. HILDEBRAND, *Reference Book of Inorganic Chemistry*, 3rd Ed. p. 394 Macmillan, New York (1951).

the following procedure was adopted. The cell was first cooled to about 2°C below the expected freezing-point, and the solute was then added and dissolved as rapidly as possible by vigorous stirring. Crystallization was then initiated by touching the outside of the cell momentarily with a small piece of dry-ice. The cell was then placed in an air-jacket at room temperature and the temperature of the cell was read as a function of time with continuous vigorous stirring of the cell contents. With careful work it was found to be possible to obtain freezing points reproducible to ±0·01°C by this method with only about 5 min total time between the addition of the solute and the attainment of the break in the "warming curve" which indicated the freezing point. This procedure was checked using potassium sulphate as the solute and was found to give satisfactory results.

Conductance measurements. The conductance measurements were carried out in a conventional manner using a Jones-Dyke type conductivity bridge. The determinations were carried out at a frequency of 1,000 c/s and a temperature of 25·0 ± 0·05°C using platinized electrodes. The cell was a modification of the Ostwald type with a cell constant of 26·92. It was of all glass construction and fitted with a mercury sealed stirrer to facilitate the dissolution of the solute. The conductance of a sample of solvent of known weight was determined, a known weight of solute was then added and the conductance of the solution was then determined.

No correction for polarization effects was made, because for reasons discussed below the inherent accuracy of the conductance measurements was quite low.

Spectra. The visible and ultra-violet spectra were taken with a Beckman DK-1 recording spectrophotometer using 1·0 cm matched silica cells fitted with ground-glass stoppers. Most of the solutions used in the spectral study were made using ordinary 98% sulphuric acid as it was found that the presence of a small amount of water did not have an appreciable effect on the observed spectra. Spectra were taken at several different concentrations and no deviation from Beer's Law was observed.

RESULTS AND DISCUSSION

The green solutions of potassium permanganate in sulphuric acid proved to be rather unstable and appear to be capable of several different modes of decomposition depending upon conditions. Solutions consisting of less than about 0·005 M permanganate in 98 per cent sulphuric acid are stable for from 24 to 36 hr when protected from reducing agents. The solution then slowly turns brown and deposits manganese dioxide. The decomposition of the solution is more rapid in solutions containing less water. Significant spectral changes occur in about 15 min when the solvent is 99·99 per cent acid. At higher permanganate concentrations the solutions become turbid and slowly deposit a green solid which decomposes to manganese dioxide as it settles. At the concentrations (about 0·01 M and up) required for the cryoscopic measurements and the conductance measurements, a visible turbidity appeared in about 5–10 min and occasionally in 1 or 2 min.*

The observation of LANKSHEAR[2d] that potassium permanganate in dilute oleum gives an unstable red-violet solution which rapidly deposits a pink solid with visible evolution of oxygen was confirmed. This change from a green to a red-violet solution which occurs sharply at essentially 100% sulphuric acid (±0·01 M water) made it necessary to work in slightly aqueous solutions rather than the 100% acid recommended by modern workers for cryoscopic and conductance measurements.[4] The amount of water present was held close to the minimum amount necessary for the repression of the self-ionization of the solvent as the presence of

* Note added in proof: W. K. Wilmarth has pointed out in a private communication that the visible turbidity appears only after 12 to 24 hr if the potassium permanganate is recrystallized before use. The author has confirmed this observation. The physical properties of the freshly prepared solutions, however, are not significantly changed by this treatment, and essentially the same changes with time are observed as when the solute is not recrystallized.

[4] R. J. GILLESPIE and E. A. ROBINSON, *Advances in Organic Chemistry and Radiochemistry* (Edited by H. J. EMELEUS and A. G. SHARPE) Vol. 1, p. 385. Academic Press, New York (1959).

larger amounts of water would only increase the uncertainties introduced by its presence.

The results of cryoscopic measurements at several concentrations of solute are shown in Table 1.

The temperatures are all reported to the nearest 0·005°C as it is felt that this is about the limit of the reliability of the method employed. The solvent freezing points reported are the average of three determinations in each case. The freezing point

TABLE 1.—RESULTS OF CRYOSCOPIC STUDIES AT SEVERAL CONCENTRATIONS OF POTASSIUM PERMANGANATE

Conc. $KMnO_4$ (Molal)	Freezing point of solvent °C	ΔT (°C)	ν
0·00358	9·885	0·120	5·8
	9·670	0·115	5·6
	9·490	0·125	6·0
	9·515	0·115	5·6
0·00650	9·475	0·215	5·6
	9·620	0·225	5·8
	9·760	0·220	5·7
0·00936	9·920	0·330	5·8
	9·575	0·330	5·8
	9·675	0·325	5·7
0·01155	9·705	0·360	5·2
	9·535	0·360	5·2
0·01277	9·830	0·340	4·5
	9·725	0·345	4·5
0·01425	9·580	0·360	4·2
	9·830	0·355	4·2

depressions, ΔT, reported at the two lowest concentrations are the average of two determinations in each case. At the higher concentrations, the solutions became turbid before a second determination could be made and each reported ΔT value is the result of a single reading. An examination of the table shows that in all cases different solutions of the same concentration gave essentially the same result, and so it is felt that the decomposition of the solutions is not markedly effecting the results.

The change of ΔT with time was followed for several of the solutions. The rate of change was not reproducible, however ΔT always decreased with time and seemed to approach a limiting value in from three to twelve hours after which no further change was observed. This limiting value corresponded approximately to the formation of four moles of particles per mole of solute.

The number of moles of particles produced by one mole of solute, ν, was calculated using the procedure of GILLESPIE *et al.*[5] and neglecting any solvation of the products. The values of ν are reported only to the nearest 0·1 unit as it is felt that this probably

[5] R. J. GILLESPIE, E. D. HUGHES and C. K. INGOLD, *J. Chem. Soc.* 2473 (1950).

is the limit of their reliability, and clearly this is sufficient accuracy for the present purposes. The solvation of the products was neglected because the changes in ν introduced by taking solvation into consideration were less than the experimental error of the measurements. A plot of ν as a function of concentration is shown in Fig. 1. These values of ν may reasonably be considered to be minimum values as any error introduced by the incomplete repression of the solvent self-dissociation would tend to decrease the experimental value of ν.

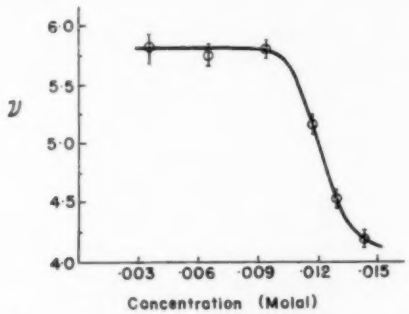

FIG. 1.—Results of cryoscopic studies at various concentration of solute. ν is the number of moles of particles found per mole of solute added. Concentration is the concentration of potassium permanganate.

The experimental values of ν found at lower concentrations of solute make it clear that at least under these conditions there are six moles of particles produced in solution by each mole of solute. Indeed due to the incomplete ionization of the water in these slightly aqueous solutions it has been shown[6] that the experimentally measured value of ν obtained under these conditions will be in general somewhat low. Using the value of GILLESPIE *et al.*[6] for the basic ionization constant of water in sulphuric acid, a theoretical "observed" value of $5{\cdot}75 \pm 0{\cdot}1$ for ν may be calculated for the solutions used here based on the assumption that one H_3O^+ ion and five other particles are produced by the dissolution of one potassium permanganate. A comparison of the observed freezing point depressions at the three lowest concentrations with the freezing point depressions observed by GILLESPIE *et al.*[6] for the oxides of nitrogen, which show this mode of ionization, shows that within the limits of experimental error the potassium permanganate freezing point depressions fall on the freezing point depression curve given by the previous authors for the oxides of nitrogen.

Thus there seems to be little doubt that the number of particles produced per mole of solute in the dilute solutions is six. The decrease of this value at higher concentrations occurs in the region of concentration where the solutions become turbid rapidly and is probably due to the partial precipitation of the products.

The conductance measurements were of a rather low order of accuracy, as in all cases some decomposition of the solution occurred before a measurement could be made. The relatively concentrated solutions required, and the time required for dissolution of the solute and equilibration of the cell contents with the constant temperature bath were such that a visible turbidity was always present at the time that measurements were obtained. A modified Ostwald type conductance cell fitted

[6] R. J. GILLESPIE, J. GRAHAM, E. D. HUGHES, C. K. INGOLD and E. R. A. PEELING, *J. Chem. Soc.* 2504 (1950).

with a mechanical stirrer was used to reduce the time required, but the first turbidity always appeared at about the time that dissolution of the solute was complete, and so no highly reliable measurements could be made. The conductance measurements were carried out on solutions approximately the same amount of water (0·06–0·10 Molal) as the solutions used in the cryoscopic studies. The high electrical conductivity of this solvent made it necessary to use somewhat higher concentrations of solute than were used in the cryoscopic studies in order to reduce the experimental error to an

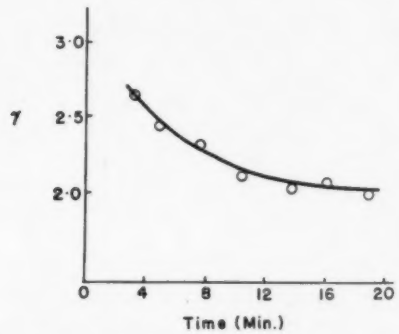

FIG. 2.—Results of a typical conductance run. γ is the apparent number of HSO_4^- ions produced by the addition of one MnO_4^- ion. Permanganate ion concentration 0·043 Molal. Temperature 25·0 ± 0·05°C.

acceptable value. The range of solute concentrations studied was from 0·04 to 0·06 M (0·022–0·033 Molal). The difference in the concentrations used in the two studies is not great and little uncertainty is introduced by this difference due to the well known nearly ideal behaviour of sulphuric acid solutions up to quite high concentrations.

The results of a typical determination are shown in Fig. 2. The results are reported in terms of the apparent number of moles of bisulphate ion produced per mole permanganate added. The amount of bisulphate ion produced was calculated on the assumption that the same amount of bisulphate ion was produced as would be produced if enough water were added to the solution to produce the observed conductance change. This procedure is justified by the very low conductance of the cations involved in sulphuric acid solutions. The conductance values of GILLESPIE and WASIF[7] for sulphuric acid–water mixtures were used.

The rate of decay of the solutions, as illustrated in Fig. 2, was not reproducible; however, the general trend was always the same. The initial value of γ, the number of moles of bisulphate ion produced per mole of solute, was always between 2·2 and 2·6, and the conductance always decreased with time to a limiting value corresponding to a γ value of 2·0 ± 0·05. No change of γ with concentration was observed over the rather narrow concentration range studied. Therefore it can be safely assumed that γ is greater 2·6 in the freshly prepared dilute solutions and its most likely upper limiting value would seem to be 3·0 as it is difficult to formulate a reasonable reaction which would result in the production of more than three bisulphate ions per added permanganate ion.

The manganese in the green solution was shown to be present in the 7+ oxidation state. The dilution of a freshly prepared green solution with a large amount of water

[7] R. J GILLESPIE and S. WASIF, *J. Chem. Soc.* 221 (1953).

and neutralization of the resulting aqueous solution leads to the quantitative recovery of the permanganate ion as determined spectrophotometrically.

Thus it would seem as though the consideration of possible reactions giving rise to the green species may be reasonably restricted to the following possiblities.

$$KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_3^+ + H_3O^+ + 3HSO_4^- \quad (1)$$

$$KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO_4SO_3H + H_3O^+ + 2HSO_4^- \quad (2)\dagger$$

$$2KMnO_4 + 3H_2SO_4 \rightarrow 2K^+ + Mn_2O_7 + H_3O^+ + 3HSO_4^- \quad (3)$$

$$KMnO_4 + H_2SO_4 \rightarrow K^+ + HMnO_4 + HSO_4^- \quad (4)$$

$$KMnO_4 + 2H_2SO_4 \rightarrow K^+ + H_2MnO_4^+ + 2HSO_4^+ \quad (5)$$

Clearly the cryoscopic and conductance measurements are consistent only with equation (1). Indeed if the probable value of $\gamma = 3$ from the conductance data is accepted along with the cryoscopic value of $\nu = 6$ the mode of ionization is shown unambiguously to be equation (1). Equation (2), however, differs from equation (1) only by the dissociation reaction

$$MnO_4SO_3H \rightleftarrows MnO_3^+ + HSO_4^-$$

and at higher concentrations and under different experimental conditions may well predominate. Indeed the failure to obtain γ values greater than 2·6 could be considered to be evidence for some association at these concentrations, however the shape of the γ vs. time curves would seem to favour the argument that this is due largely to decomposition of the solution.

The cryoscopic results at higher concentrations and the change of conductance with time, as shown in Figs. 1 and 2, then become explainable if the turbidity is considered to be due to precipitation of the salt $(MnO_3)(HSO_4)$ or the undissociated species MnO_4SO_3H. The complete precipitation of the manganese in either of these forms would of course lead to the values $\nu = 4$ and $\gamma = 2$. This would make it appear that both the cryoscopic and the conductance measurements were actually carried out on supersaturated solutions and were possible only because of the well known sluggishness of reactions in this very viscous medium.

Cryoscopic, conductance, and spectral studies were attempted on the red-violet dilute oleum solutions; however, no reproducible results were obtained. It would appear that the decomposition of these solutions is too rapid for meaningful results to be obtained by the procedures employed.

Additional information concerning the nature of these solutions can be obtained by an examination of their visible and ultra-violet absorption spectra, the observed absorption maxima of which are given in Table 2.

TABLE 2.—ABSORPTION MAXIMA OF THE VISIBLE AND ULTRA-VIOLET SPECTRUM OF $KMnO_4$ DISSOLVED IN H_2SO_4

Freq (cm^{-1})	ε_{max}	Transition assignment
15,900	105	$a_2'n$–$e''\pi^*$
21,500	465	$a_2'n$–$a_1'\sigma_1^*$
33,300	6,500	$a_2'n$–$e'\sigma^*$
>48,000 (end ab.)	>18,000	—

† This formulation is suggested by unpublished work by W. K. WILMARTH. The author wishes to thank a Referee for bringing this to his attention.

These are all smooth, relatively symmetrical peaks which show none of the fine structure characteristic of the spectrum of aqueous permanganate solutions.

This relatively simple spectrum can be shown to be consistent with the expected electronic structure of a planar trigonal MnO_3^+ ion of symmetry D_{3h}. An LCAO treatment of this ion gives the gives the following electronic structure

$$(A)(L)(a'\sigma)^2(e'\sigma)^4(e''\pi)^4(a_2''\pi)^2(e'\pi')^4(a_2'n)^2\dagger$$

with the lowest energy excited levels being $e''\pi^*$, $a_1'\sigma_1^*$, and $e'\sigma^*$. A consideration

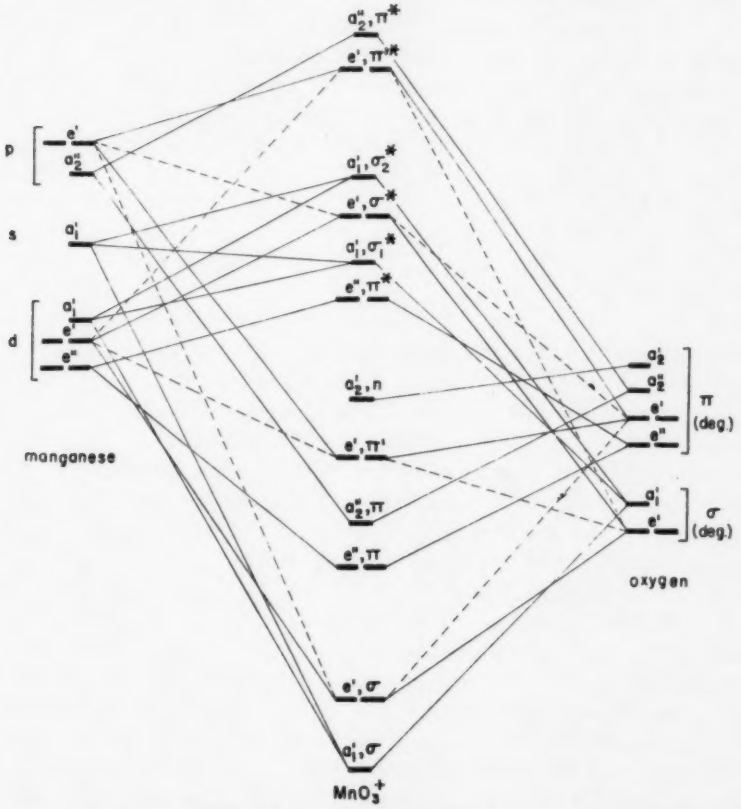

FIG. 3.—Schematic representation of the proposed electronic structure of the permanganyl ion. The orbitals designated $e'\pi'$ and $e'\pi'^*$ are located in the plane of the atoms and are thus not directly comparable with the remaining π-orbitals.

of the electronic structure of the permanganate ion[8,9] and the SO_3 molecule[10] (which is geometrically similar to the proposed MnO_3^+) would seem to make the energy order given above and illustrated schematically in Fig. 3 the most probable order. There is little doubt in the order of the molecular orbitals up through $a'n$ except that the relative energies of $a'\sigma$ and $e'\sigma$ are rather uncertain. These σ-bonding

† (A) and (L) represent the core electrons of the manganese and the ligands respectively.

[8] M. WOLFSBERG and L. HELMHOLTZ, *J. Chem. Phys.* **20**, 837 (1952).
[9] C. J. BALLHAUSEN and A. D. LIEHR, *J. Mol. Spectroscopy* **2**, 342 (1958).
[10] A. D. WALSH, *J. Chem. Soc.* 2301 (1953).

orbitals would however be expected to lie at a considerably lower energy than any of the other levels under consideration and it seems very unlikely that transitions involving these levels will appear in the spectrum. Mixing of the four e' levels might lower the energy of the $e'\pi'$ level sufficiently so that it would lie at a lower energy than the $a_2''\pi$ orbital despite the less favourable overlap involved; however, this seems to be rather unlikely. The observed spectrum is compatible with both arrangements and both will be considered as there is no information available to distinguish between the two possibilities.

The relative energies of the first three excited levels $e''\pi^*$, $a_1'\sigma_1^*$ and $e'\sigma^*$ are rather uncertain. These are essentially perturbed *d*-orbitals on the central manganese and the order given in Fig. 3 is that normally produced by a trigonal field.[11] The interaction of the e'' atomic orbitals may however be strong enough to make the $e''\pi^*$ molecular level lie above the $a_1'\sigma_1^*$ orbital thus making the order $a_1'\sigma_1^*$, $e''\pi^*$, $e'\sigma^*$.

A consideration of the possible one electron transitions involving the three highest filled energy levels and the three lowest excited levels reveals the following: $a_2'n \rightarrow e''\pi^*$, $a_2'n \rightarrow a_1'\sigma_1^*$, and $a_2''\pi \rightarrow e'\sigma^*$ are symmetry forbidden; $e'\pi' \rightarrow e''\pi^*$ and $a_2''\pi \rightarrow a_1'\sigma_1^*$ are allowed and give rise to excited states of symmetry A_2''; and $a_2'n \rightarrow e'\sigma^*$, $e'\pi' \rightarrow a_1'\sigma_1^*$, $e'\pi' \rightarrow e'\sigma^*$ and $a_2''\pi \rightarrow e''\pi^*$ are allowed and give rise to excited states of symmetry E'.

The low intensity of the band at 15,900 cm^{-1} would indicate that it is probably a forbidden transition and may reasonably be assigned to either $a'_2n \rightarrow e''\pi^*$ or $a_2'n \rightarrow a_1'\sigma_1^*$ depending on which of the excited states lies at the lower energy. The band at 21,500 cm^{-1} could be assigned to either a forbidden transition with an unusually great intensity or to an allowed transition with a low transition probability. The first of these two possibilities would seem to be the more probable provided that the abnormally great intensity of this normally forbidden transition can be explained. The non-totally symmetric vibrations of this species are of the symmetry a_2'', e' and e' giving rise to vibronic excited states E' and A_2'' for the transition $a_2'n \rightarrow e''\pi^*$, and A_1'' and E' for the transition $a_2'n \rightarrow a_1'\sigma_1^*$. Thus if the allowed transition which occurs at 33,300 cm^{-1} is the transition $a_2'n \rightarrow e'\sigma^*$ the $e'\sigma^*$ level will lie above the $e''\pi^*$ and $a_1'\sigma_1^*$ levels by only 11,800 cm^{-1} and 17,400 cm^{-1}, and the two lower energy transitions would both be expected to show a significant intensity due to vibronic mixing with the allowed transition.[12] It is difficult to make a realistic estimate of the expected intensity of these bands as the vibrational frequencies involved are not known. Estimates of the ratios of the intensity of the allowed transition and the forbidden transitions, using reasonable values for the parameters involved[13] shows that the observed intensities of the forbidden bands are at least of the proper order of magnitude. The end absorption at $>48{,}000$ cm^{-1} could then be assigned any of the following transitions $e'\pi' \rightarrow e''\pi^*$, $e'\pi' \rightarrow a_1'\sigma_1^*$, $a_2''\pi \rightarrow e''\pi^*$ or $a_2''\pi \rightarrow a_1'\sigma_1^*$ or to an overlapping of several of these depending upon the relative energies of the $e'\pi'$ and $a_2''\pi$ levels and of the $e''\pi^*$ and $a_1'\sigma_1^*$ levels. Thus the observed spectrum is consistent with the assumed structure of the permanganyl ion.

While there are undoubtedly species of different composition and symmetry which would be expected to give rise to similar spectra, their presence in these solutions

[11] C. J. BALLHAUSEN and C. K. JØRGENSEN, *Kgl. Danske Videnskab, Selskab Mat. fys. Medd.* **29**, No 14 (1955).
[12] H. SPONER and E. TELLER, *Revs. Mod. Phys.* **13**, 76 (1941).
[13] G. HERZBERG and E. TELLER, *Z. Physik. Chem.* B **21**, 410 (1933).

seems rather unlikely. A consideration of the spectra expected for the other manganese (VII) species which might reasonably be expected to be present (MnO_4SO_3H, $HMnO_4$, and Mn_2O_7) shows that none of these species would be expected to give rise to the observed spectrum. These species would all be expected to have the general structure $ROMnO_3$ with the local symmetry at the manganese being no higher than C_{3v}. An examination of the behaviour of the low energy transitions of the permanganate ion of symmetry T_d upon the reduction of the symmetry to C_{3v} reveals the following. The lowest energy transitions in the permanganate ion are, according to BALLHAUSEN and LIEHR,[9] $t_1\pi \rightarrow e^a\pi$, $t_1\pi \rightarrow t_2{}^{a_1}\sigma$, and $t_2{}^{a_1}\pi \rightarrow e^a\pi$ in order of increasing energy. The first of these splits into two components, the second into four components, and the third into two components when the symmetry is reduced to C_{3v}, and all eight of the resultant transitions are allowed transitions. Thus if a species of this type is responsible for the observed spectrum the low intensity band observed at 15,900 cm^{-1} must be assigned to an allowed transition. There is no apparent reason why any of these transitions should have an abnormally low transition probability, and thus such an assignment would seem to be very unlikely. Therefore it is not at all likely that the observed spectrum is due to a species of the form $ROMnO_3$. Thus the $MnO_3{}^+$ ion of symmetry D_{3h} is the only species which might reasonably be expected to give rise to the observed spectrum which is likely to occur in this system.

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Acknowledgement—The author wishes to thank Dr. W. H. EBERHARDT for helpful discussions concerning the interpretation of the spectra.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 168 to 173. Pergamon Press Ltd.

A PORTION OF THE SYSTEM NH_3–V_2O_5–H_2O AT 30°C

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(*Received* 28 *July* 1960)

Abstract—A portion of the phase diagram has been completed for the system NH_3–V_2O_5–H_2O at 30°C. Ammonium hexavanadate, $(NH_4)_2V_6O_{16}$, and ammonium metavanadate, NH_4VO_3, are the only stable solid phases in the area studied. A number of other ammonium polyvanadate compounds have been reported in the literature. All of these appear to be unstable with respect to ammonium hexavanadate or else do not exist at 30°C. The solubility isotherm indicated only a limited solubility for pentavalent vanadium in ammonium hydroxide solutions at 30°C. A maximum solubility of 1·8 weight % V_2O_5 was observed.

A MINIMUM of reliable information is available on the solubility of pentavalent vanadium in ammonium hydroxide solutions or on the composition and number of solid ammonium vanadates. A survey of the literature reveals a number of references pertaining to solid ammonium vanadates; however, few of them have been well identified and some contradiction exists between various articles. Therefore, it was deemed advisable to establish independently the existence of these compounds.

The following ammonium vanadates, listed in order of increasing mole ratio of NH_3 to V, have been reported in the literature:

$10V_2O_5 \cdot 3(NH_4)_2O \cdot 15$ or $18H_2O$;[1,2]
$3V_2O_5 \cdot (NH_4)_2O$ or $(NH_4)_2V_6O_{16}$;[2,3,4]
$7V_2O_5 \cdot 3(NH_4)_2O \cdot 4H_2O$;[3]
$2V_2O_5 \cdot (NH_4)_2O \cdot 4H_2O$;[6]
$V_2O_5 \cdot (NH_4)_2O$ or NH_4VO_3.[3,4,8]
$13V_2O_5 \cdot 4(NH_4)_2O \cdot 18$ or $22H_2O$;[1,2]
$5V_2O_5 \cdot 2(NH_4)_2O \cdot 5H_2O$;[2,5]
$2V_2O_5 \cdot (NH_4)_2O \cdot 2\frac{1}{2}H_2O$;[2,5]
$5V_2O_5 \cdot 3(NH_4)_2O \cdot 6H_2O$;[2,7]

In all but two cases, identification of these solid phases was based solely on chemical analyses. CALVO[6] reported that $(NH_4)_2V_4O_{11} \cdot 4H_2O$ precipitated from a boiling solution of ammonium metavanadate and established that there are eighteen vanadium atoms in the unit cell. A crystal study of ammonium metavanadate NH_4VO_3, was completed by LUKESH[8]. The unit cell is orthorhombic and contains four formula weights. The structure is composed of VO_4 tetrahedra.

EXPERIMENTAL

Samples containing varying amounts of ammonia, V_2O_5 and water were equilibrated at constant temperature. The solubility isotherm was established by direct chemical analysis of the saturated

[1] J. BELTRAN and C. GUILLEM, *An. Real. Soc. Espan. Fis. y Quim.* **53** B, 745 (1957).
[2] J. BELTRAN and C. GUILLEM, *An. Real. Soc. Espan. Fis. y Quim.* **53** B, 735 (1957).
[3] J. W. MELLOR, *Inorganic and Theoretical Chemistry*, pp. 757–760. Longmans, Green (1928).
[4] M. LACHARTRE, *Bull. Soc. Chim.* **35**, 321 (1924).
[5] J. BELTRAN and C. GUILLEM, *An. Real. Soc. Espan. Fis. y Quim.* **52** B, 215 (1956).
[6] C. CALVO. Ph.D. Thesis, Rutgers University (1954).
[7] I. LINDQUIST, Communication to ROSSOTTI and ROSOTTI, *Acta Chem. Scand.* **10**, 983 (1956).
[8] J. S. LUKESH, *Acta Cryst.* **3**, 476 (1950).

solutions produced by equilibration. The identity of the solid phases was determined by comparing the X-ray powder diffraction pattern of selected samples of the solids with known patterns of various ammonium vanadates. Extrapolation of the tie-lines in the phase diagram gave results in agreement with those obtained by X-ray diffraction.

It is known that four points which are associated with each sample lie on a straight line when plotted on triangular co-ordinates. These points are the composition of the starting mixture, the saturated solution, the wet residue, and the solid phase. In the method of SCHREINEMAKERS,[9] tie-lines are drawn through the saturated solution and wet residue composition points for a number of samples having varying ratios of the constituents. These are extended to their point of convergence, this point being the composition of the solid phase. HILL and RICCI[10] proposed two improvements on SCHREINEMAKERS' wet residue method. In most systems the components which are used to prepare the starting mixture can be weighed or buretted with more accuracy than the wet residue can be analysed. Therefore, they recommend using the starting mixture and saturated solution points to establish the tie-lines. SCHREINEMAKERS' method of geometric extrapolation of the tie-lines is limited by the size of the graph paper and accuracy with which the lines can be drawn. HILL and RICCI recommended a method of algebraic extrapolation to test the convergence of the tie-lines. This method has the advantage of being limited only by the accuracy of the determination of the starting mixture and saturated solution points. HILL and RICCI's method of algebraic extrapolation involving the composition of the starting mixture and saturated solution was followed in this work to determine the composition of the solid phase.

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Various combinations of compounds containing ammonia and V_2O_5 can be used in the experiments; however, the rate of attaining steady state may differ with the choice of materials. The following combinations were tested by equilibrating samples for various periods of time, with the indicated results.

1. $(NH_4)_2V_6O_{16} + H_2O$—produced colloidal solutions
2. $(NH_4)_2V_6O_{16} + NH_4OH + H_2O$—produced colloidal solutions
3. $V_2O_5 + NH_4VO_3 + H_2O$—produced colloidal solutions
4. $NH_4VO_3 + H_2O$—steady state established in one day
5. $V_2O_5 + NH_4OH + H_2O$—steady state established in 3–4 days

The combinations of V_2O_5, NH_4OH, and H_2O produced clear solutions and no further change in the concentration of vanadium in solution was observed after 3–4 days, i.e., the samples had reached steady state. In addition, these starting substances can be varied to cover the entire phase diagram. They were chosen as the starting materials.

Pure V_2O_5 was prepared for use in these tests by the following procedure. Purified V_2O_5 was dissolved in a hot sodium carbonate solution and filtered to remove insoluble impurities. Ammonium metavanadate, precipitated by the addition of ammonium chloride, was washed, air-dried and decomposed at 400°C for several hours to produce V_2O_5. Chemical analysis indicated that it was at least 99·8% V_2O_5 with no vanadium(IV) present. A spectrographic analysis showed only the following impurities: 0·002% Cu, 0·005% Fe, 0·0005% Mg, 0·002% Mn and 0·01% Si.

The samples were prepared by placing the appropriate weight of V_2O_5 and volumes of NH_4OH and H_2O in screw-cap bottles or sealed ampoules at the higher ammonia concentrations. They were continuously agitated in a shaking thermostat maintained at 30·0 ± 0·1°C. After equilibration the saturated solution was sampled by drawing a portion through a glass-wool plug into a pipette. The solid phase was collected on a funnel, washed lightly with H_2O and air-dried. Selected samples were subsequently examined by X-ray diffraction techniques.

The composition of the starting mixture was calculated on the basis of the weight of V_2O_5 taken and the volume and known density[11] of water and standardized aqueous ammonia used.

The composition of the saturated solution was obtained by chemical analyses in grammes per litre. This value was converted directly to weight percent since the density of NH_4VO_3 solutions are very close to 1·00 at all concentrations.[12] The vanadium was analysed by acidifying the solution with H_2SO_4, $KMnO_4$ was added to insure complete oxidation of the vanadium, the excess $KMnO_4$ was destroyed with a dilute $NaNO_2$ solution, the excess $NaNO_2$ was destroyed with urea and the

[9] F. A. H. SCHREINEMAKERS, *Z. Phys. Chem.* **11**, 81 (1893).
[10] A. E. HILL and J. E. RICCI, *J. Amer. Chem. Soc.* **53**, 4306 (1931).
[11] *International Critical Tables* III, 59 (1928).
[12] *International Critical Tables* III ,70 (1928).

TABLE 1.—EXPERIMENTAL DATA

Initial mixture		Saturated solution		Solid phase	
w% V_2O_5	w% NH_3	w% V_2O_5	w% NH_3	By tie-line extrapolation	By X-ray
3·85	0·23	colloidal			$(NH_4)_2V_6O_{16}$
3·77	0·24	colloidal			
3·94	0·24	colloidal			
3·97	0·27	colloidal			
3·86	0·27	0·34	0·04		
4·01	0·30	0·38	0·04		
4·23	0·30	0·49	0·06		
3·86	0·28	0·58	0·11		$(NH_4)_2V_6O_{16}$
3·58	0·33	0·68	0·12		
3·96	0·38	0·68	0·13		
3·86	0·41	0·69	0·12		$(NH_4)_2V_6O_{16} + NH_4VO_3$
3·92	0·43	0·68	0·13		
3·87	0·50	0·70	0·13		
3·85	0·52	0·68	0·12		$(NH_4)_2V_6O_{16} + NH_4VO_3$
3·85	0·54	0·68	0·12		
3·58	0·54	0·84	0·13		
4·00	0·60	0·68	0·12		
3·85	0·60	0·79	0·14		
3·85	0·62	0·66	0·12		$(NH_4)_2V_6O_{16} + NH_4VO_3$
3·83	0·65	0·84	0·14		
3·87	0·77	0·63	0·17	NH_4VO_3	
3·87	0·77	0·61	0·15	NH_4VO_3	
3·87	0·82	0·63	0·18	NH_4VO_3	
3·87	0·82	0·64	0·18	NH_4VO_3	
3·87	0·88	0·63	0·23	NH_4VO_3	
3·87	0·93	0·64	0·29	NH_4VO_3	
3·87	0·93	0·68	0·31	NH_4VO_3	
3·87	0·99	0·68	0·38	NH_4VO_3	
3·87	0·99	0·66	0·38	NH_4VO_3	
3·87	1·04	0·68	0·43	NH_4VO_3	
3·87	1·04	0·71	0·44	NH_4VO_3	
3·88	1·10	0·71	0·50	NH_4VO_3	
3·88	1·10	0·75	0·50	NH_4VO_3	
3·87	1·10	0·71	0·53	NH_4VO_3	
3·88	1·15	0·75	0·52	NH_4VO_3	
3·88	1·15	0·76	0·57	NH_4VO_3	
4·27	1·28	0·85	0·63	NH_4VO_3	NH_4VO_3
3·88	1·38	0·86	0·81	NH_4VO_3	
3·88	1·38	0·87	0·84	NH_4VO_3	
4·48	1·78	1·15	1·20	NH_4VO_3	
3·88	1·75	1·00	1·23	NH_4VO_3	
5·00	2·05	1·04	1·26	NH_4VO_3	NH_4VO_3
3·89	2·04	1·11	1·54	NH_4VO_3	
4·81	2·15	1·25	1·55	NH_4VO_3	
5·69	2·66	1·25	1·88	NH_4VO_3	
5·09	3·85	1·75	3·4	NH_4VO_3	NH_4VO_3
6·40	5·53	1·76	4·6	NH_4VO_3	

TABLE 1—(*continued*)

Initial mixture		Saturated solution		Solid phase	
w%V_2O_5	w%NH_3	w%V_2O_5	w%NH_3	By tie-line extrapolation	By X-ray
5·55	5·95	1·78	5·4	NH_4VO_3	
5·49	5·99	1·70	5·9	NH_4VO_3	
5·64	6·90	1·80	6·2	NH_4VO_3	
6·16	7·49	1·80	6·6	NH_4VO_3	NH_4VO_3
6·95	8·34	1·70	7·7	NH_4VO_3	
5·22	8·49	1·63	8·1	NH_4VO_3	
6·26	9·65	1·56	9·4	NH_4VO_3	NH_4VO_3
4·14	10·1	1·55	9·9	NH_4VO_3	
6·04	10·9	1·38	10·3	NH_4VO_3	
7·98	13·2	1·25	12·2	NH_4VO_3	
5·66	13·5	1·20	12·7	NH_4VO_3	

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vanadium was then titrated potentiometrically with a standard ferrous ammonium sulphate solution. The ammonia was determined by standard Kjeldahl techniques.

The information obtained is presented in Table 1. The composition of the starting mixture and saturated solution were calculated as described above. The solid phase was identified by algebraic extrapolation of the tie-lines or by X-ray diffraction techniques. The X-ray diffraction patterns were obtained with filtered chromium K_α radiation using Debye–Scherrer cameras. The solubility isotherm is shown in Fig. 1 and 2.

DISCUSSION

The data show that NH_4VO_3 and $(NH_4)_2V_6O_{16}$ are the only stable solid ammonium vanadates in the area studied. In the metavanadate region this is clearly supported by X-ray diffraction patterns of the solid phases, as well as by extrapolation of the tie-lines. In the polyvanadate region the existence of ammonium hexavanadate is shown by X-ray diffraction patterns of the solids and is supported by the shape of the solubility isotherm. Algebraic extrapolation of the tie-lines was not successful in this region due to the small angle subtended by the hexavanadate portion of the solubility isotherm. Only one isothermal invariant point is seen where the solid changes from metavanadate to hexavanadate.

Since only ammonium hexavanadate is observed, all the other ammonium polyvanadates which have been reported must be unstable with respect to it or else do not exist at 30°C. These other ammonium polyvanadates are usually obtained by evaporation of acidified ammonium metavanadate solutions. The author has prepared the compound $5V_2O_5 \cdot 3(NH_4)_2O \cdot 6H_2O$ by that technique. It is not a physical mixture of metavanadate and hexavanadate, as shown by the X-ray pattern, and it is not an equilibrium solid, as shown by the phase diagram.

Some of these other polyvanadates may be related to the ions in solution. It has been shown by potentiometric titrations,[13,14,15] conductometric titrations[16] and spectrophotometric investigations[17] that vanadium is polymerized in acidified solutions, probably as a decavanadate. Evidence for a decavanadate and not multiples

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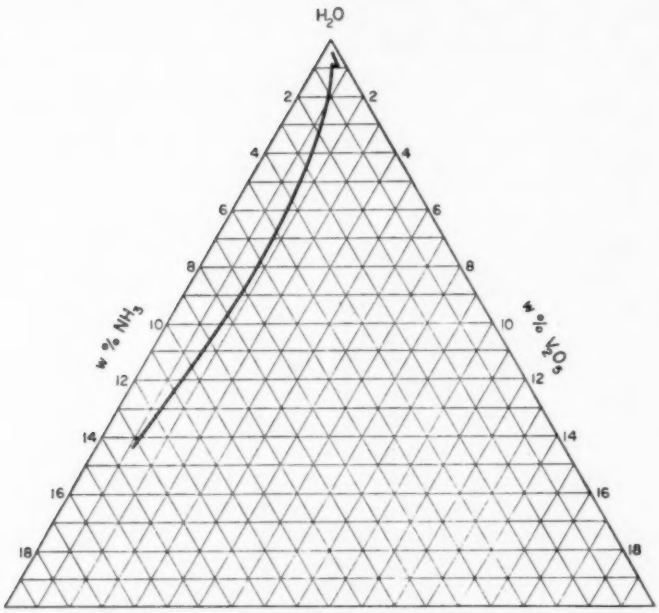

FIG. 1.—The system NH_3–V_2O_5–H_2O 30°C solubility isotherm.

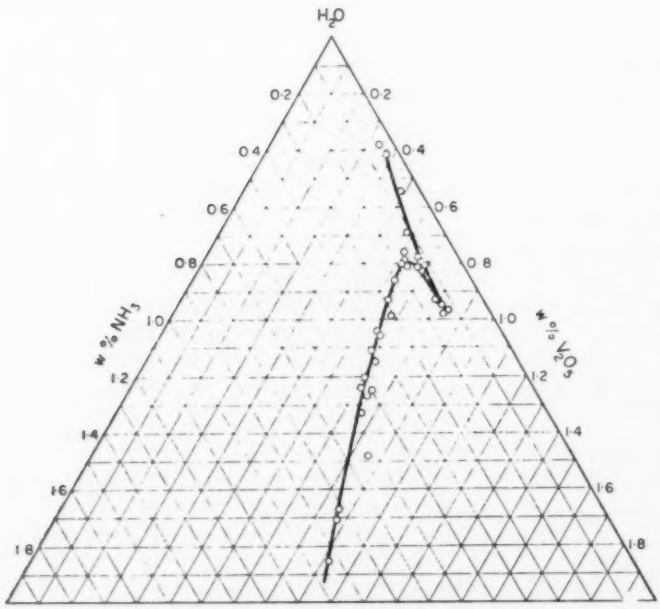

FIG. 2.—Low ammonia region of the system NH_3–V_2O_5–H_2O 30°C solubility isotherm.

thereof have been found by salt-cryoscopic measurements,[18] ultracentrifuge techniques,[19] and vapour-pressure measurements.[20] The most definitive work, by ROSSOTTI and ROSSOTTI,[15] suggests the following equilibria:

$$10VO_2^+ + 8H_2O = H_2V_{10}O_{28}^{4-} + 14H^+$$
$$H_2V_{10}O_{28}^{4-} = HV_{10}O_{28}^{5-} + H^+$$
$$HV_{10}O_{28}^{5-} = V_{10}O_{28}^{6-} + H^+$$

It could be postulated that the compounds having mole ratios of $NH_3/V = 0{\cdot}4$, $0{\cdot}5$ and $0{\cdot}6$ are solids related to the $H_2V_{10}O_{28}^{4-}$, $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$ ions, respectively. This is not well supported by the available information. The $NH_3/V = 0{\cdot}60$ compound[2,7] and $0{\cdot}4$ compound[2,5] have been identified by chemical analysis only and the $NH_3/V = 0{\cdot}5$ compound[6] contained eighteen vanadium atoms per unit cell, not ten as might be expected if it was formed from decavanadate units.

In the potassium system EVANS[21] noted that KV_3O_8 was stable with respect to $K_6V_{10}O_{28}{\cdot}9H_2O$. When he evaporated an acidified potassium metavanadate solution red crystals of $K_6V_{10}O_{28}{\cdot}9H_2O$ were formed. However, when the crystals were allowed to age in contact with the mother liquor they disappeared and orange KV_3O_8 was formed. He concluded that the decavanadate was an intermediate in the formation of KV_3O_8.

The solubility isotherm, Figs. 1 and 2, shows that vanadium has a limited solubility in NH_4OH solutions. When sufficient excess NH_4OH is present a maximum solubility of 1·8 weight % V_2O_5 was achieved. The solubility of vanadium at a composition of one mole of NH_3 per mole of V, equivalent to ammonium metavanadate, was 0·6 weight % V_2O_5. This is in good agreement with data for the solubility of ammonium metavanadate.[22,23] It was not possible to extend the solubility isotherm to the point corresponding to pure V_2O_5. At very low ammonia concentrations colloidal solutions were encountered. This was probably due to a colloidal dispersion of V_2O_5. It has been reported that V_2O_5 can be dispersed in water simply by grinding and the solubility of V_2O_5 in water was stated to be 0·125 weight per cent.[24] If this figure is correct, then in this small region where the solubility isotherm could not be determined it should pass through another invariant point and decrease to the value for V_2O_5.

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NOTES

High-resolution infra-red spectrum of the $[Fe(CN)_5NO]^{2-}$ ion

(*Received* 8 *August* 1960)

INFRA-RED spectral data on the crystalline sodium nitroprusside, $Na_2[Fe(CN)_5NO].2H_2O$, have been published earlier by MILLER and WILKINS[1] and by HERINGTON and KYNASTON[2]. They observed only one band in the C N stretching region at frequencies of 2140 and 2152 cm^{-1} respectively, and one absorption band attributable to the N O stretching vibration, at 1925 and 1938 cm^{-1}, respectively. These studies were performed, however, by the use of a rock-salt prism and the accuracy of the frequency data was quoted[2] to be only 10 cm^{-1}. The far infra-red region of the spectrum was recently published by MILLER *et al.*[3]

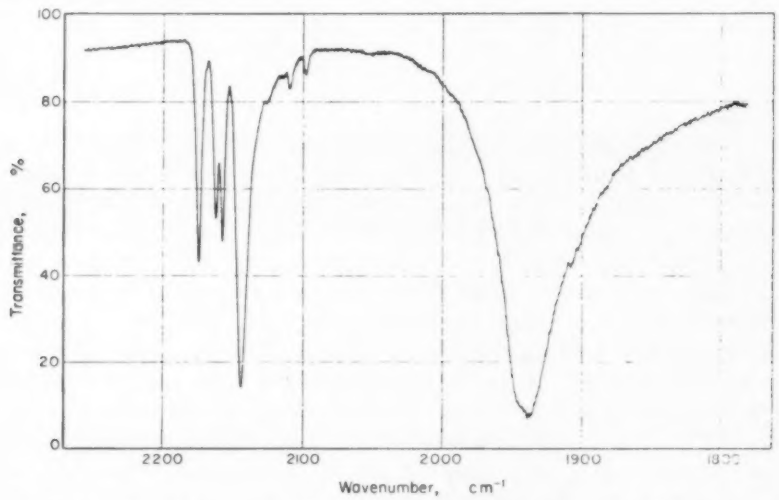

FIG. 1.—Infra-red spectrum of $Na_2[Fe(CN)_5NO].2H_2O$ in the C N and N O stretching region (Nujol mull).

The inadequate resolution of a rock-salt prism for the study of the X Y stretching vibrations in the 2000 cm^{-1} region was recently demonstrated in studies of the spectra of some metal carbonyls.[4,5]

Supposing that the $[Fe(CN)_5NO]^{2-}$ ion belongs to the point group C_{4v} it could be shown[6] that this symmetry demands three C N stretching modes (two of the species A_1 and one of species E), and one N≡O stretching fundamental which are active in the infra-red. Using a simple single-beam spectrometer with a LiF prism we observed these four bands and reported earlier the following frequencies:[6] 2174, 2159, 2141 and 1940 cm^{-1}.

Meanwhile COTTON *et al.*[7] reported also four absorption bands, correct for the point group C_{4v}, but at the frequencies 2182, 2155, 2169 and 1944 cm^{-1}.

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Recently we reinvestigated the spectrum of the crystalline $Na_2[Fe(CN)_5NO].2H_2O$ in the spectral range between 1800–2300 cm^{-1}. The positions of the absorption maxima could be determined with higher accuracy than earlier, and due to the high spectral resolution it could be observed, that the second C≡N stretching band is split into two branches (Fig. 1). This may be caused by the effect of the crystal field, and if so, these bands shall be assigned to the degenerate normal mode of vibration ν_{16}.

The frequencies of the absorption maxima of the fundamental bands in a Nujol mull are shown in Table 1. Additional weak bands or shoulders were observed at 2133, 2125·7, 2109·5, 2098·4 and 1909 cm^{-1}.

TABLE 1.—FREQUENCIES OF THE C≡N AND N≡O STRETCHING VIBRATIONS OF CRYSTALLINE $Na_2[Fe(CN)_5NO].2H_2O$ IN A NUJOL MULL

Vibration	Species	Frequency (cm^{-1})	Assignment
ν_1	A_1	2173·4	CN stretch., symm.
ν_{16}	E	2161·6 2156·7	CN stretch., deg.
ν_2	A_1	2143·4	CN stretch., antisymm.
ν_3	A_1	1939 ± 1	NO stretch.

For sake of comparison we reinvestigated the triply degenerate infra-red active CN stretching bands of $K_4[Fe(CN)_6]$ and $K_3[Fe(CN)_6]$ too, under the same conditions. The broad absorption band of the Fe(II) complex has an asymmetric shape and contains several sub-maxima. A discussion of these has already been given by BONINO *et al.*[8,9] We observed the frequency of the highest absorption at 2040 ± 1 cm^{-1}.

The absorption band of the Fe(III) complex is much narrower and has one sharp sub-maximum. The frequency of the absorption maximum is at 2116·0 cm^{-1}, that of the sub-maximum at 2119·8 cm^{-1}. CAGLIOTI *et al.*[10] reported the frequency value of 2125 cm^{-1} for this compound.

Comparing the C≡N stretching frequencies of these three ions, and keeping in mind the well known correlation, according to which an increase of the oxidation number of the central atom in cyanogen and carbonyl complexes increases the C≡N and C≡O stretching frequencies, one can draw the same conclusion as HERRINGTON and KYNASTON,[2] i.e. that the Fe atom in the nitroprosside ion has a formal oxidation state of Fe^{III} or even Fe^{IV}.

A discussion of the high CN frequency values in sodium nitroprusside was given recently by EL-SAYED and SHELINE,[11] on the basis, however, of poorly resolved spectra,[2] whereas LEWIS *et al.*[12] studied thoroughly the bonding problems of transition metal–nitric oxide complexes from the point of view of the NO stretching vibrations.

According to our spectral data it is felt that the concept of bonding of the NO group in the form of an NO^+ ion may only be formally true and is an oversimplification of the real electronic distribution, which is, at present, not fully understood.

Experimental

Spectra were recorded by the full-automatic double-beam spectrometer UR 10 of VEB Carl Zeiss, Jena, using the LiF prism. Spectral slit width values, wave number calibration and scanning characteristics were the same as reported earlier.[1] The CN stretching frequencies are accurate within ±0·1 cm^{-1}.

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Preparation and properties of lanthanum and cerium diiodides[1]

(*Received* 1 *September* 1960)

METAL–METAL halide systems for the lighter lanthanons show a considerable variance in the degree of apparent solution of the metals in their molten chlorides and iodides. In La–$LaCl_3$, a solubility of 9% mole metal in the liquid salt at the eutectic (826°), and 15% at 914° has been found,[2] while solution of 9·3% metal at the monotectic (777°) and 9·7% at 950° has been reported in Ce–$CeCl_3$.[3] In both systems only the solid metal and trichloride separate on cooling. The increased solubility of praseodymium in $PrCl_3$, 17·1% at the eutectic, is accompanied by the formation of the slightly-stable, solid $PrCl_{2\cdot2}$, and, in Nd–$NdCl_3$, an even more extensive reaction results in the formation of solid $NdCl_2$ as well as $NdCl_{2\cdot2_7}$ and $NdCl_{2\cdot3_7}$.[4] A low melting neodymium diiodide, somewhat analogous to that of samarium, and some indication of a lower iodide of praseodymium have also been reported earlier.[4]

It has now been established that even lanthanum and cerium form stable and essentially stoicheiometric diiodides and that these are quite different from those of neodymium and samarium. The systems La–LaI_3 and Ce–CeI_3 have been investigated as before[4] by thermal analysis and by equilibration experiments. The triiodides have been prepared from the reaction of iodine with the metals[5] in a tungsten crucible, and, in the case of lanthanum, subsequently sublimed *in vacuo* to remove a small carbon impurity. The metal turnings were stored in evacuated containers and only briefly exposed to air during transfer; the salts were handled only in vacuum or under argon in the dry box. Impurities, particularly oxygen, have a very considerable effect on the phase results.

Reduction of LaI_3, m.p. 778°, proceeds substantially quantitatively to LaI_2, $LaI_{2\cdot04\pm0\cdot02}$ having been obtained on four equilibrations with excess metal at 790 to 815°; the diiodide melts slightly incongruently at 820°. Similarly, CeI_3, m.p. 766°, is reduced to CeI_2 (<2·06 I/Ce obs), which at 799 ± 3° is in equilibrium with liquid metal and a melt of composition $CeI_{2\cdot09}$. These systems closely parallel the behavior of Pr–PrI_3 investigated earlier,[4] where solid $PrI_{2\cdot01\pm0\cdot01}$ melts at 758° to $PrI_{2\cdot15(l)}$ and $Pr_{(s)}$. All three systems also exhibit an intermediate compound; these have, in two cases, been identified as $CeI_{2\cdot4}$, peritectic 731°, and $PrI_{2\cdot5_9}$, m.p. 676°.

The diiodides of lanthanum and cerium, as well as praseodymium, are all isomorphous and distinctly different from the other lanthanon(II) iodides, for example, in their high melting points (compare β–NdI_3, 787°, NdI_2–, 562°[4]) and in their general metallic appearance, which shades from blue-black with LaI_2 to bronze for PrI_2. The metal-like character is confirmed by their high conductivities; $\frac{3}{16}$ in. to $\frac{1}{4}$ in. thick, polycrystalline pieces of the three, as recovered from phase studies, have gross resistances of only 1–3 ohms, and some of this appears to be at the probe contact. In contrast, neodymium diiodide is definitely a good insulator. As might be expected from this, qualitative susceptibility measurements indicate that LaI_2 is diamagnetic.

As a result we are inclined to view these compounds as containing not M^{+2} ions but rather the normal tripositive ions together with an equal number of electrons in essentially metallic bonding with the cations, i.e., $M^{+3}e^-(I^-)_2$. A similar situation has been suggested for the brassy-yellow CeS,[6] and for the gray, metallic $LaC_2(La^{+3}e^-C_2^=)$;[7] in both cases resistivities were found to be comparable to those of the metals. Analogous dicarbides are found throughout the lanthanons, except that YbC_2, in the absence of H_2 evolution of hydrolysis, appears to be a truly divalent actylide like the isostructural CaC_2.[8] However, there is no apparent precedent among other halides for the behaviour of these iodides.

In view of the differences of opinion regarding the nature of metals when dissolved in their molten

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halides in general, and in $CeCl_3$ in particular,[4,9-11] a comparison of the electrical properties of the present MI_3–MI_2 melts with those of the conducting, solid diiodides should be particularly informative.

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Absorption spectra of solid UCl_4 and $UOCl_2$*

(*Received* 26 *September* 1960)

IN a recent investigation of the tetravalent uranium chlorides, the absorption spectra of the anhydrous salts, UCl_4 and $UOCl_2$, were determined by preparing a mull of the solids in petrolatum. The qualitative data show some interesting differences between these two compounds.

Experimental

Materials

Anhydrous uranium tetrachloride was prepared by refluxing a suspension of UO_3 in hexachloropropene in accordance with the procedure given by PITT *et al.*[1]. Final purification of the compound was accomplished by vacuum distillation. The product was analysed for uranium and chlorine by standard volumetric procedures. (Found: U, 62·58; Cl 37·18%. Calc. U, 62·67 F; Cl, 37·33%).

Anhydrous uranous oxychloride ($UOCl_2$) was prepared and purified in accordance with the procedure of KRAUS[2,3] and analysed by the same methods used for the UCl_4. (Found: U, 74·3; Cl, 21·2 %. Calc.: U, 73·25; Cl, 21·87 %.) The X-ray diffraction pattern of the material did not correspond with the patterns for UCl_4 or UO_2.

Procedure

A mull in petrolatum was prepared for each compound by grinding 0·1 g of the anhydrous salt with 1 g of petrolatum under a dry atmosphere. The mull was placed on one of the polished faces of a one centimeter spectrophotometer cell. A plug of polished quartz 0·9 cm^2 on the end and a length slightly greater than the height of the cell was inserted. The mull was forced into the void space making a light path through the mull of 0·1 cm. The absorption spectra were obtained with a Cary Model 14 spectrophotometer using a mull of calcium carbonate in the reference beam. The amount of calcium carbonate in the mull was adjusted to provide a blank having sufficient optical density and light scattering properties to balance the instrument.

Results

The absorption spectra of the anhydrous solids, UCl_4 and $UOCl_2$, were obtained and are shown as curves B and C respectively in Fig. 1. The absorption spectra for U(IV) in concentrated hydrochloric acid is shown as curve A for comparison. The three spectra show the prominent absorption bands of tetravalent uranium at 600–700 mμ and 1000–1200 mμ.

* Work performed under contract No. AT(45-1)-1350 for the U.S. Atomic Energy Commission.

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Of particular interest here is the absorption spectrum of the $UOCl_2$ solid which shows the appearance of a new band between 1250 and 1350 mμ and the fine structure on the 1000–1200 mμ band. The fine structure probably results from a vibrational mode of the uranium–oxygen bond.

The $UOCl_2$ was not soluble in nitromethane, acetone, tributyl phosphate, dibutyl phosphate, phosphorous oxychloride, ether and pyridine but did dissolve in water, acids and molten pyridinium chloride. However, dissolution apparently occurs only with reaction as the absorption spectra of the dissolved $UOCl_2$ in the latter solvents was typical of the spectra of similar solutions containing UCl_4.

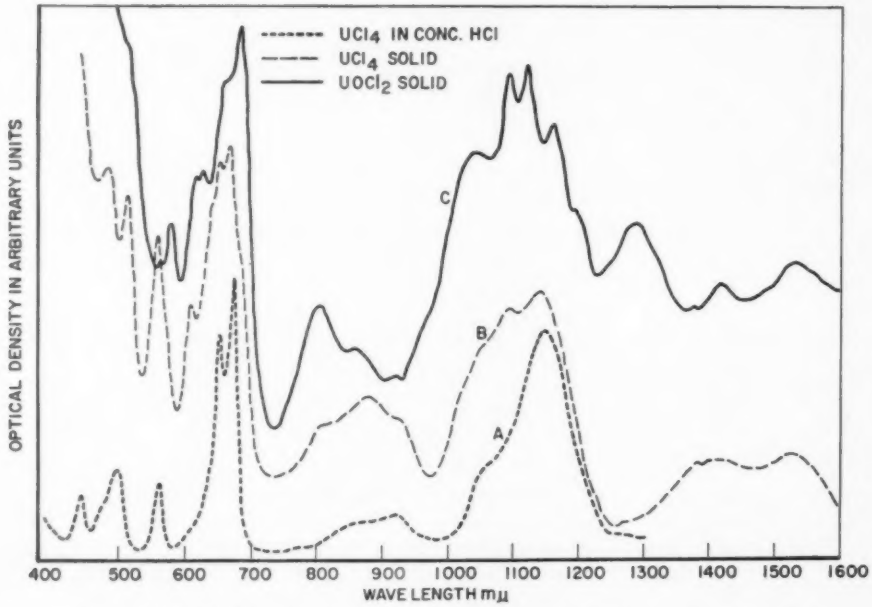

FIG. 1.—Absorption spectra of solid UCl_4 and $UOCl_2$ mulled with petrolatum and of UCl_4 in conc HCl.

In pyridium chloride the dissolved species was the hexachlorouranate(IV). In hydrochloric acid the spectrum was identical to that of dissolved UCl_4, while in water the distinctive spectrum of U(IV) polymer was observed. In every case when $UOCl_2$ dissolved, the characteristics of uranium(IV) chloride solutions were observed. This strongly implies that the uranium–oxygen bond in $UOCl_2$ is stabilized only in the solid state probably by the lattice energy of the crystal.

Acknowledgement—The author wishes to thank the members of Analytical Laboratories Operation under E. W. CHRISTOPHERSON for performing the analyses of the materials.

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The α/β branching ratio of ^{241}Pu*

(*Received* 14 *September* 1960)

THE α/β disintegration ratio of ^{241}Pu has been recently remeasured by BROWN *et al.*[1], who report a value of $2{\cdot}31 \pm 0{\cdot}06 \times 10^{-5}$. Previously reported values have ranged from $1{\cdot}9$ to $4{\cdot}5 \times 10^{-5}$. This

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] F. BROWN, G. G. GEORGE, D. E. GREEN and D. E. WATT, *J. Inorg. Nucl. Chem.* **13**, 192 (1960).

communication describes a recent measurement of this ratio by slightly different methods at this laboratory. The value obtained was $2{\cdot}31 \pm 0{\cdot}10 \times 10^{-5}$. Partial β- and α-half-lives of $13{\cdot}3 \pm 0{\cdot}3$ years and $5{\cdot}6 \pm 0{\cdot}2 \times 10^{5}$ years were measured.

The plutonium used had the following isotopic composition: ^{239}Pu, 1·37%; ^{240}Pu, 2·24%; ^{241}Pu. 96·19%; and ^{242}Pu, 0·20%. Of the total plutonium alphas, 2·5% were due to ^{238}Pu.

Measurements were made on three different samples prepared from the plutonium stock solution. The samples were purified from americium, uranium, and neptunium by an initial fluoride precipitation, followed by adsorption on an anion column in strong HCl, reduction with HI, and elution from the column. The plutonium was then oxidized with bromate and extracted into diethyl ether. After back-extraction with water, samples were directly evaporated or electroplated on platinum for α- and β-counting, comparison fission counting, or α-pulse analysis.

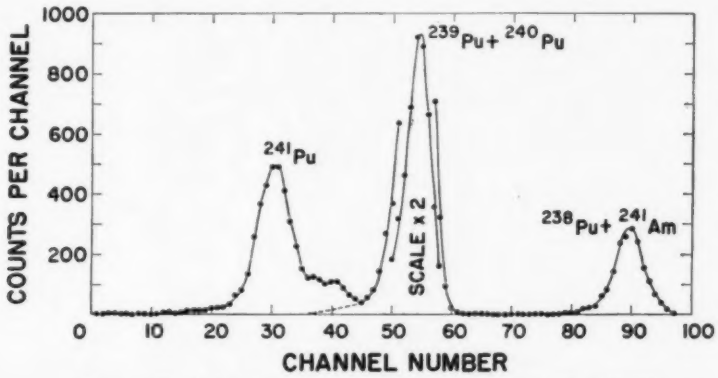

FIG. 1.—Typical α-spectrum taken 2·1 days after chemical purification.

The ^{241}Pu β-decay rate of each sample was measured in terms of the α growth. ^{241}Am was the only α-emitter growing in, as shown by α-pulse analysis. The ^{241}Pu α-decay rate was determined in two different ways. In two of the samples the ^{241}Pu alphas were observed directly; in the third, the absolute β-decay rate of the daughter ^{237}U was measured at various times up to equilibrium.

α-Counts were taken daily in a zinc sulphide scintillation counter and a methane-flow proportional counter, and plotted versus time since americium separation. Extrapolation back to time of separation gave the total Pu α-decay rate, and the initial slope gave the ^{241}Am growth rate.

Sample no. 1, directly evaporated from solution, and sample no. 2, electroplated, were α-pulse analysed in a Frisch-gridded ionization chamber filled with approximately one atmosphere of argon with 1% carbon dioxide. A typical α-spectrum is shown in Fig. 1. The small multiple peak at approximately 5·0 MeV is due to the combined effect of low-intensity α-transitions to low-lying levels of ^{237}U, and coincidence between conversion electrons and high-intensity α-groups. In the resolution of the spectrum, the "tailing" function for ^{239}Pu + ^{240}Pu was assumed to be similar to that of the ^{241}Am peak, and is indicated by the broken line. Good agreement in the ^{241}Pu/total Pu α ratio for the two samples was obtained, in spite of a considerable difference in the magnitude of the "tail" correction.

Sample no. 3 was purified and electroplated, then β-counted daily in a thin-window methane-flow proportional counter. Its β-count rate grew to equilibrium with the ^{237}U half-life (6·75 days). The equilibrium disintegration rate of ^{237}U was calculated using a counting efficiency previously determined by 4π counting and by growth of ^{237}Np, and checked by mass spectrometry.

The data are summarized in Table 1. The ^{241}Pu branching ratio is given exactly by the expression

$$\frac{^{241}\text{Pu}\alpha}{^{241}\text{Pu}\beta} = \frac{^{241}\text{Pu } \alpha\text{-disintegration rate}}{\left(\frac{1}{\lambda_{\text{Am}}} \times \text{Am growth rate}\right) + \text{Am decay rate}}$$

In this calculation the second term in the denominator, the Am decay rate, was neglected, since it was $\leqslant 10^{-4}$ of the first.

Probably the greatest source of error in the first two branching ratios calculated is the interpretation of the α-pulse analyses. Any errors other than statistical in the α counting are systematic, and tend to cancel, since the α disintegration rate appears in both numerator and denominator of the equation. An uncertainty of 5 per cent is therefore assigned to the first two ratios. In the third determination, the ^{237}U counting efficiency is subject to the greatest error, and an uncertainty of 7% is assigned to the ratio based on ^{237}U. An average α/β branching ratio for ^{241}Pu is calculated to be $2{\cdot}31 \pm 0{\cdot}10 \times 10^{-5}$.

The α- and β-half-lives of ^{241}Pu could have been calculated using data already at hand, by using a combination of α-counting, pulse analysis, and mass spectrometry to calculate the atoms of ^{241}Pu

TABLE 1

	α-Branch			β-Branch	Ratio
Sample	ΣPuα (dis/min) (α-counters)	$\frac{^{241}\text{Pu}\alpha}{\Sigma\text{Pu}\alpha}$ (pulse analyser)	^{241}Puα (dis/min)	Am growth rate (α dis/min per day) (α-counters)	$\frac{^{241}\text{Pu}\alpha}{^{241}\text{Pu}\beta}$
1	914	0·279	255	46·27	$2{\cdot}31 \times 10^{-5}$
2	8897	0·280	2490	453·4	$2{\cdot}31 \times 10^{-5}$
3	4869	—	1360 (equals ^{237}U dis/min at equilibrium)	247·0	$2{\cdot}32 \times 10^{-5}$

present. However, since the ^{239}Pu and ^{240}Pu were minor constituents, it seemed advisable to avoid possible systematic errors in the mass spectrometry by determining the ^{241}Pu by an independent method. Since ^{241}Pu has a high thermal cross-section, it can be determined by comparison of its fission counting rate with that of another thermal fissioner in the same neutron flux, provided that the number of atoms on the standard plate and the relative cross-sections are known. Foil no. 2 was measured in a fission counter in the Los Alamos Water Boiler versus standards of ^{235}U and ^{239}Pu. Cross-sections were corrected for a neutron temperature of 63°C, using cross-sections and correction factors calculated by WESTCOTT[2].

This foil was found to have $1{\cdot}088 \times 10^{15}$ atoms of ^{241}Pu on it, which gives β- and α-half-lives of $13{\cdot}3 \pm 0{\cdot}3$ and $5{\cdot}62 \pm 0{\cdot}20 \times 10^{5}$ years, both in good agreement with the measurements of BROWN *et al.*[1]

Acknowledgements—The author wishes to thank L. F. KRENZIEN for the mass spectrometry, T. T. SHULL for the fission counting, and Drs. J. D. KNIGHT and G. A. COWAN for their interest and valuable suggestions.

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[2] C. H. WESTCOTT, CRRP-787, Revision (1958).

Half-life of 134*m* Cs and the cross-section for its formation by neutron activation*

(*Received* 27 *October* 1960)

THE thermal neutron cross-section of 133 Cs to produce 134*m* Cs has been redetermined to have a value of $2{\cdot}44 \pm 0{\cdot}15$ barns. (All errors quoted here are standard deviations). The half-life of 134*m* Cs

* Work performed under the auspices of the U.S. Atomic Energy Commission.

also has been redetermined and has a value of 2·895 ± 0·005 hr. The cross-section value obtained is markedly larger than an earlier published value[1] of 17 mb, since at the time the latter was determined the γ-transition branch of 134*m* Cs was unknown, and only the β-decay branch which represents ~1 per cent of the total disintegrations was measured.[2] BAERG and BARTHOLOMEW[3] recently obtained a tentative value of 3·0 barns. HUGHES *et al.*[4] list a value of 3·0 ± 0·3 barns taken from work done at Chalk River.

Experimental

"Specpure" (Johnson Matthey Co.) Cs_2CO_3 was used for all irradiations, and no significant impurities were found present in the short (~15 min) irradiations employed. For the six cross-section determinations, weighed amounts of the Cs_2CO_3 were dissolved in volumetric flasks, and known aliquots were taken to give accurately known samples of about 0·1 mg. These were sealed in polyethylene film and irradiated for 15 min in the VG-7 facility of the Materials Testing Reactor, where the

TABLE 1.—HALF-LIFE OF 134*m* Cs

Experiment no.	Type of counter	Half-life (hr)
1	γ-spectrometer	2·885
2	γ-spectrometer	2·886
3	γ-spectrometer	2·896
4	γ-spectrometer	2·914
5	γ-spectrometer	2·896
Average γ-half-life	2·895 ± 0·005* hr	
6	β-scintillation	2·911
7	β-proportional	2·910
8	β-proportional	2·896
9	β-proportional	2·915
10	β-proportional	2·933
Average β-half-life	2·913 ± 0·006* hr	

* Standard deviation of the mean.

thermal flux is approximately 10^{13} n/cm² per sec, and the experimental Cd ratio for 40 mil Co wire and 40 mil Cd is ~35. A Co wire flux monitor (80 mg) was included with each sample. Each Cs sample was counted at least twice at known time intervals after its removal from the reactor. A NaI(Tl) crystal scintillation counter connected to a 256 channel analyser was used for counting. The absolute geometry and counting efficiency of the system have been determined by HEATH.[5] The activity of the 127 keV photopeak was measured and the data converted to absolute disintegration rate by means of the value (7·0 ± 0·2 dis/γ) of the number of disintegrations for each 127 keV gamma emitted given by KEISCH and YATES.[6] The Co flux monitors were counted in a high pressure ionization chamber which operates with a precision of ±0·5 per cent. Thermal neutron flux measurements made by this method have an absolute error[7] of ±5% with the half-life of ^{60}Co taken as 5·28 ± 0·06 years and the thermal neutron activation cross section of ^{59}Co taken as 36·3 ± 1·5 barns. Two of the samples were irradiated with a 20 mil Cd cover to determine the effect of epi-Cd neutrons.

For half-life determinations samples were irradiated in a similar manner and after dissolution were further purified by a $Fe(OH)_3$ scavenging treatment followed by the precipitation of $BiI_3 \cdot CsI$. After washing, the precipitate was treated with a NaOH solution which converts the precipitate to $Bi(OH)_3$ and dissolves the Cs. The precipitate was removed and a sample was prepared by evaporation of the supernate on a glass plate. Ten samples were prepared by this method. Five samples were β-counted, one with an anthracene crystal scintillation counter and four with an end window flow-type proportional counter. The decay rate was observed at 36 points over about 4 half-lives. The tail due

(1) L. SEREN, H. N. FRIEDLANDER and S. H. TURKEL, *Phys. Rev.* **72**, 888 (1947).
(2) A. W. SUNYAR, J. W. MIHELICH and M. GOLDHABER, *Phys. Rev.* **95**, 570 (1954).
(3) A. P. BAERG and R. M. BARTHOLOMEW, AECL Report PR-CM-18 (1959).
(4) D. J. HUGHES, B. A. MAGURNO and M. K. BRUSSEL, BNL Report BNL-325 (2nd Ed.) p. 15 (1958).
(5) R. L. HEATH, USAEC Report IDO-16408 (1957).
(6) B. KEISCH and E. A. C. YATES, *J. Inorg. Nucl. Chem.* To be published (1961).
(7) C. HOGG, USAEC Report IDO-16538 (1960).

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to 2·3 year ^{134}Cs amounted to ~1·6 per cent of the counting rate at the beginning of the decay measurements and ~50 per cent at the end of the measurements, and this was subtracted. The remaining five samples were counted on the γ-scintillation spectrometer. The decay of the 127 keV peak was followed by taking a total of 35–40 points over a period of at least 4·7 half-lives. The ^{134}Cs Compton background amounted to ~0·05 per cent of the total counts in the peak at the beginning of the decay measurements and ~1·5 per cent at the end of the measurements and was subtracted from each point.

TABLE 2.—NEUTRON ACTIVATION CROSS-SECTION FOR THE FORMATION OF 134*m* Cs

Experiment no.	Type	Cross-section (barns)
1	reactor spectrum	2·65
2	reactor spectrum	3·10
3	reactor spectrum	2·80
4	reactor spectrum	2·85
5	effect of epi-Cd neutrons	0·41
6	effect of epi-Cd neutrons	0·41
	average for reactor spectrum	2·85
	mean, thermal neutrons	2·44 ± 0.09 (standard deviation of the mean)
Thermal neutron cross-section		2·44 ± 0·15 (errors considered in Table 3)

TABLE 3.—ERRORS CONSIDERED IN CROSS-SECTION DETERMINATION

Source of error	Standard deviation (%)
Absolute flux determination	5
Geometry and efficiency of NaI scintillation counter	03
Resulting from epi-Cd effect	0·5
Number of atoms in sample	0·1
Irradiation time	3·1
Disintegration/127γ	
Counting statistics	0·5
Half-life of 134*m* Cs	0·1
Total error	6·2

Results

Weighted-least-squares analyses of the decay data were made with the aid of an IBM 650 computer and yielded the values for the half-life of 134*m* Cs shown in Table 1. These may be compared with the previous measurements of 3·15 ± 0·2 hr given by SLATIS,[8] who determined the half-life by following the β-decay of a sample produced by activation with cyclotron neutrons. The result of the γ-decay determinations (2·895 ± 0·005 hr) is to be regarded as the better of the two reported here because of the better statistics resulting from higher γ-counting rates and the smaller background corrections for the 2·3 year ^{134}Cs component.

The results of the cross-section determinations are shown in Table 2. The errors involved are listed in Table 3. The average result is stated as 2·44 ± 0·15 barns for the thermal cross-section after subtraction of the contribution of the non-thermal neutrons.

Acknowledgement—The assistance of LEWIS HANSEN in carrying out the IBM weighted least squares analyses is gratefully acknowledged.

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[8] H. SLĀTIS, *Arkiv Matematik, Astronomi, Fysik* **32A**, No. 16 (1945).

Conversion coefficients for the 127 keV transition in the decay of ^{134m}Cs*

(*Received* 27 *October* 1960)

In determining the neutron activation cross-section[1] for formation of ^{134m}Cs it was desirable to count the unconverted γ-rays of the 127 keV transition as a measure of activation. Since a large fraction of this transition occurs by emission of conversion electrons, it was necessary to know the ratio (dis/γ) of the total disintegration rate to the 127 keV γ-emission rate. Calculation of this ratio from previously published conversion coefficients yields a value of 8·1 which is inexact because of errors involved. A value for the K conversion coefficient, of 2·6 $\pm$ 0·3 was reported by Sunyar *et al.*[2] and the $K/L/M$ ratio, 23/34/6, reported by Caldwell[3] contains no estimate of errors except the statement by the author that the ratios are only approximate. A direct determination of the dis/γ ratio therefore seemed appropriate. By use of a $4\pi\beta$–γ coincidence counting technique the ratio has been determined to have the value 7·0 $\pm$ 0·2 dis/γ. In the course of the work the K conversion coefficient was redetermined, and the resulting value, 2·60 $\pm$ 0·04, agrees very well with that previously reported.[2] The errors stated are standard deviations.

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Procedure

^{134m}Cs was produced by irradiating "Specpure" Cs_2CO_3 (Johnson Matthey Co.) in the VG–7 facility of the Materials Testing Reactor. For the $4\pi\beta$–γ coincidence sources, ~0·01 mg of material was irradiated for 2 hr. It was then dissolved and an aliquot containing 0·2–0·4 μg of material was deposited (by evaporation under a heat lamp) on ~0·5 cm² of a VYNS film ~5 μg/cm² thick having a gold coating ~20 μg/cm² thick. This source was counted in a $4\pi\beta$–γ coincidence counter described by Yates[4].

The decay scheme[2] of ^{134m}Cs shows that ~99+ % of the ^{134m}Cs atoms decay by isomeric transition through a cascade consisting of a 127 keV transition followed by a 10 keV transition; in the latter transition the gammas are nearly completely[2] converted ($\alpha_L \sim 200$). The 5 keV L-conversion electrons emitted in this latter step are in coincidence with the 127 keV transition. The number of coincidences divided by the 127 keV γ-counting rate gives the efficiency of the $4\pi\beta$-counter for counting the 5 keV L-conversion electrons, and this was found to be ~90 per cent. Therefore the small fraction (~1/7) of undetected disintegrations which make the first (127 keV) transition via γ-emission are subsequently counted with 90 per cent efficiency, resulting in an overall efficiency for detecting disintegrations of 98–98·5 per cent. This assumes that the $4\pi\beta$-counter detects the conversion electrons from the first transition with nearly 100 per cent efficiency. (Even if the latter efficiency is as low as 90 per cent the overall efficiency remains within the limits given.) The same sources were counted within 20 min, in a scintillation spectrometer of standard geometry given by Heath,[5] to obtain the 127 keV γ-emission rate. The disintegration and 127 keV γ-emission rates were corrected for decay to a common time using the value of 2·90 hr for the half-life reported by Keisch[1].

For the determination of α_K approximately 0·1 mg of Cs_2CO_3 was irradiated for 15 min and counted on the scintillation spectrometer described above. The total counts in the 30 keV Cs K X-ray and the 127 keV γ-peaks were compared, with corrections made for geometry and efficiency,[5] peak-to-total ratio,[5] absorption in the crystal container and absorber[5] (added to exclude electrons), iodine X-ray escape phenomena,[6] and loss due to Auger electron production.[7]

Results

Three determinations of dis/γ, (disintegrations per 127 keV gamma emitted) were made, and the results were 7·0, 6·9, and 7·2. The average is 7·0 $\pm$ 0·2. The errors involved in these and the following determinations are listed in Table 1.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

[1] B. Keisch, *J. Inorg. Nucl. Chem.* To be published (1961).
[2] A. W. Sunyar, J. W. Mihelich, and M. Goldhaber, *Phys. Rev.* **95**, 570 (1954).
[3] R. L. Caldwell, *Phys. Rev.* **78**, 407 (1950).
[4] E. A. C. Yates, USAEC Report IDO–16580 p. 40 (1960).
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[6] P. Axel, USAEC Report BNL–271 (1953).
[7] A. H. Wapstra, G. J. Nijgh and R. Van Lieshout, *Nuclear Spectroscopy Tables* pp. 81, 82. Interscience New York (1959).

TABLE 1—ERRORS CONSIDERED IN THE DETERMINATIONS

dis/γ Measurement	Error (%)
Counting statistics ($4\pi\beta$-count)	0·1
Efficiency calculation	0·5
Counting statistics (γ-count)	2
Geometry and efficiency (γ-count)	2
Peak-to-total ratio (γ-count)	0·5
Absorption (γ-count)	0·5
Iodine X-ray escape (γ-count)	0·5
Half-life of ^{134m}Cs (γ-count)	0·1
Total error	3
K Conversion coefficient measurement	
Counting statistics (both peaks)	1
Geometry and efficiency	0·1
Peak-to-total ratio	0·5
Absorption	0·5
Iodine X-ray escape	0·5
Fluorescence yield	0·6
Total error	1·5

Two determinations of α_K (K conversion coefficient) were made and the results were 2·63 and 2·57 The average is 2·60 $\pm$ 0·04.

It should be noted that SLIV[8] and ROSE[9] predict $\alpha_K = 2{\cdot}6$ for this E3 transition.[2] From our data the sum $L/K + M/K$ (ratios of numbers of L and M to K electrons emitted) may be calculated as 1·31 $\pm$ 0·05. CALDWELL[3] obtains the approximate values $L/K = 1{\cdot}5$ and $M/K = 0{\cdot}2$ for a sum of 1·7. ROSE[9] predicts $L/K = 1{\cdot}1$ and $M/K = 0{\cdot}6$ giving 1·7 for the sum. SLIV[10] predicts $L/K = 1{\cdot}2$.

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[8] L. A. SLIV and I. M. BAND, *Coefficients of the Internal Conversion of Gamma Radiation; Part* I, *K-Shell*. USSR Academy of Sciences, Moscow–Leningrad (1956).
[9] M. E. ROSE, *Internal Conversion Coefficients*, pp. 62, 63, 147. Interscience, New York (1958).
[10] L. A. SLIV and I. M. BAND, *Coefficients of the Internal Conversion of Gamma Radiation*: *Part* II, *L-Shell*. USSR Academy of Sciences, Moscow–Leningrad (1958).

On the reaction of metal carbonyls with sodium-borohydride

(*Received* 3 *November* 1960)

IT HAS been suggested[1] that the ability of certain amines to cause the disproportionation of iron pentacarbonyl is dependent upon the availability of the lone pair of electrons on nitrogen (polar effect) and the presence of steric groups which prevent electrons from reaching the reaction site. We now wish to report that the borohydride ion can react with metal carbonyls to cause a similar reaction.

[1] H. W. STERNBERG, R. A. FRIEDL, S. L. SHUFLER and I. WENDER, *J. Amer. Chem. Soc.* **77**, 2675 (1955).

The reaction proceeds smoothly at room temperature and can be carried out with relative ease compared with the use of sodium in liquid ammonia as method of producing metal carbonyl anions.[2]

Experimental

Using standard vacuum line techniques[3] a standard tapered flask was charged with a sodium borohydride–diglyme slurry under an atmosphere of nitrogen. The flask was attached to the vacuum line, the nitrogen was removed, and the slurry was degassed by cooling and warming several times. The iron pentacarbonyl was added to the slurry through a side arm stopcock attached to the flask. The reaction was instantaneous as evidenced by the formation of a deep red solution and an immediate pressure increase. After several minutes no further increase in pressure was noted. The gaseous product passed a −196° trap and was found to be a mixture of hydrogen and carbon monoxide.

The spectrum of the red solution in the carbonyl frequency region (4·5–5·5 μ) was found to be quite complex and positive identification of any single iron carbonyl species was not possible. Removal of the solvent from this solution yielded a pyrophoric red solid which has been reported previously.[4] These investigators have also reported a deep red solution formed in a few days by the reaction of $Fe(CO)_5$ and aqueous NaOH. The red solution exhibited a broad absorption band at 5400 Å.

Acidification of the red solution yielded a dark green solid whose infra-red (2047, 2020, 1832 cm^{-1}) and visible (6070 Å) spectra were identical with those of iron tetracarbonyl.[5] That this was the product was confirmed by analysis. (Found: 33·6. Calc. for $Fe_3(CO)_{12}$: Fe, 33·3). It is interesting to note that the red solution can be regenerated from $Fe_3(CO)_{12}$ and $NaBH_4$ suggesting that this solution may contain ions of the trimer, $Fe_3(CO)_{11}^{-2}$ or $HFe_3(CO)_{11}^{-1}$.[6] Furthermore, the infra-red spectrum of the red solution was identical with that prepared from $Fe(CO)_5$ and $NaBH_4$. It was also observed that $NaBH(OCH_3)_3$ can replace $NaBH_4$ in the reaction; however, the reaction time for the formation of the red solution was longer (approx. 4–8 hr).

Similarly, $NaBH_4$ reacted with $Co_2(CO)_8$ in triglyme to give a light yellow solution which gave a strong peak at 1886 cm^{-1} which has been reported to be due to the anion, $Co(CO)_4^{-1}$.[7] The hexacarbonyls of chromium, molybdenum and tungsten also reacted with $NaBH_4$ in triglyme to give a red, yellow and yellow solutions, respectively. Such solutions probably contain ions of the type $M(CO)_5^{-2}$ as reportedly formed from these carbonyls and sodium in liquid ammonia.[2]

Acknowledgements—The authors are indebted to Antara Chemicals, New York, for a generous supply of iron pentacarbonyl. The subject matter of this paper is covered by pending patent applications owned by Allis-Chalmers Mfg. Co., Milwaukee, Wisconsin.

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[2] H. BEHRENS, *Z. Anorg. Chem.* **291,** 122 (1957).
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[4] H. W. STERNBERG, R. MARKBY and I. WENDER, *J. Amer. Chem. Soc.* **79,** 6116 (1957).
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[6] W. HIEBER and G. BRENDEL, *Z. Anorg. Chem.* **289,** 524, (1957).
[7] W. F. EDGELL *et al.*, *J. Amer. Chem. Soc.* **82,** 1254 (1960).

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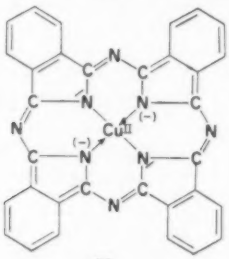
J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 186 to 192. Pergamon Press Ltd.

LETTERS TO THE EDITOR

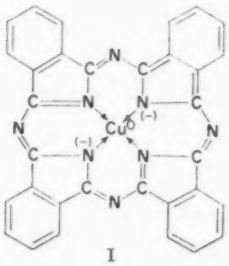
Copper(O) phthalocyanine

(*Received* 15 *August* 1960)

IN a recent paper under the above title, WATT and DAWES[1] described the reduction of copper(II) phthalocyanine with potassium in liquid ammonia to an anion "$[Cu^0PC]^{--}$". We wish to point out that it is not possible to assert, on the basis of the evidence presented by these authors, that the product



II



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must be regarded as a Cu(O) rather than a Cu(II) derivative. Indeed it would appear that the structures (I) and (II) corresponding to these two alternative formulations represent two of the possible resonance forms of this anion; thus the oxidation state of the central metal atom is in this case not only undetermined but indeterminate.

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[1] G. W. WATT and J. W. DAWES, *J. Inorg. Nucl. Chem.* **14**, 32 (1960)

A new pentasilicon dodecachloride, Si_5Cl_{12}[1]

(*Received* 26 *September* 1960)

EARLIER workers[2,3] have reported liquid substances with compositions corresponding to that of Si_5Cl_{12}. These substances were characterized solely by elemental analysis.

In the preparation of Si_6Cl_{14} reported previously[4] it was found that if large amounts of amine were used in promoting the disproportionation of Si_2Cl_6 to $Si_6Cl_{14}\cdot SiCl_4$ and Si_6Cl_{14} some of the amine was usually entrained in, or complexed with, the solid product. In the subsequent sublimation, required for the purification of Si_6Cl_{14}, small amounts of a more volatile crystalline solid were obtained along with Si_6Cl_{14}. Similarly, if pure resublimed Si_6Cl_{14} is brought into contact with trimethylamine vapour and then heated at 70–80° *in vacuo*, again this more volatile solid is produced along with $SiCl_4$ and a yellow crystalline non-volatile solid.

Better yields of this new sub-chloride can be obtained using the reaction system illustrated in Fig. 1. The apparatus is evacuated and disilicon hexachloride is distilled into tube (A), maintained at −196°.

[1] The authors are grateful for the generous financial assistance of the Alfred P. Sloan Foundation in pursuance of the research here reported.
[2] A. BESSON and L. FOURNIER, *C.R. Acad. Sci., Paris* **148**, 834 (1909); *Ibid.* **149**, 34 (1909).
[3] G. MARTIN, *J. Chem. Soc.* **105**, 2836 (1914).
[4] A. KACZMARCZYK and G. URRY, *J. Amer. Chem. Soc.* **82**, 751 (1960).

An amount of trimethylamine greater than twice the number of moles of Si_2Cl_6 used is then distilled into U-tube (B) which has been cooled to −196° following the distillation of the Si_2Cl_6 into tube (A). After these distillations have been completed the reaction system is closed from the vacuum system. Tube (A) is then allowed to warm to 0° at the same time that U-tube (B) is allowed to warm to −79°. During the ensuing disproportionation the $SiCl_4$ formed diffuses from Tube (A) into U-tube (B)

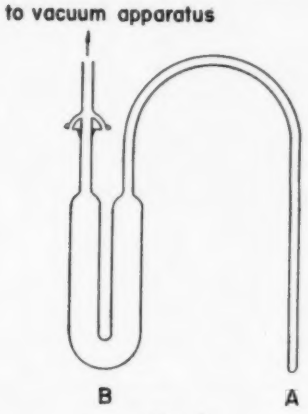

FIG. 1.

through a constantly maintained vapour-pressure of trimethylamine. When there is no more liquid remaining in tube (A)[5] the reaction system is again opened to the vacuum apparatus and the material volatile *in vacuo* at room temperature removed. This consists of $SiCl_4$ and most of the amine used originally. There remains in the reaction system a solid with the composition of Si_6Cl_{14} mixed with the remainder of the amine. This solid is then heated to 70° and maintained at a pressure of 10^{-5} mm for several hours.[6] During this pyrolysis the $SiCl_4$ formed is removed continuously along with the liberated amine; in addition, clear colourless crystals sublime from the heated zone. The pyrolysis is continued until the formation of $SiCl_4$ ceases and no more sublimate is obtained.

The volatile crystalline solid was characterized and identified as Si_5Cl_{12} by means of elemental analysis, the hydrogen produced upon alkaline hydrolysis, and by molecular weight determination.

Analysis; (Found: Si, 24·9; Cl, 75·3%. Calc. for Si_5Cl_{12}: Si, 24·8; Cl, 75·2%).

Hydrogen produced upon alkaline hydrolysis; (Found: 159 cc at STP/ g. Calc. for Si_5Cl_{12}: 158 cc at STP/ g).

Molecular weight; A sample weighing 0·202 g exerted a pressure of 34·2 mm in a volume of 336 cc at a temperature of 244° corresponding to a molecular weight of 567. Calc. for Si_5Cl_{12}, 565·8.

The new (isomer of) Si_5Cl_{12} melts sharply at 347 ± 2° but solidifies slowly into a glass upon cooling from this temperature. This glass crystallizes over a period of months at room temperature.

Pentasilicon dodecachloride exhibits the following vapour-pressures:[7]

t°C	170	180	190	200	210	220	235
$p$mm	3·5	5·2	7·9	11·6	17·1	21·1	33·2

Si_5Cl_{12} is moderately soluble in $SiCl_4$. When such a solution is cooled to −45° and the material volatile at that temperature and a pressure of 10^{-5} mm is removed, there remains a complex of the composition Si_5Cl_{12}·$SiCl_4$. This 1:1 molar complex affords a simple and extremely accurate method of titrating Si_5Cl_{12}.

[5] Depending upon the amount of Si_2Cl_6 used this may be a period of from 1 to 5 days.

[6] At this temperature and pressure Si_6Cl_{14} does not sublime at a visible rate. If the temperature is allowed to climb as high as 120°, however, Si_6Cl_{14} does sublime and appears to be the major product.

[7] These vapour-pressures are open to some question since there are indications of a reaction which occurs slowly between mercury and Si_5Cl_{12} when vapours of the latter are allowed to stand in contact with the former for long periods of time at temperatures in excess of 200°.

Pentasilicon dodecachloride reacts with anhydrous HCl at room temperature producing a mixture of $SiHCl_3$ and $SiCl_4$ along with traces of hydrogen and Si_2Cl_6. The reaction is essentially complete in 24 hr.

We are continuing investigations of the properties of this new substance with a particular interest in the structure. The fact that it melts at a higher temperature than Si_6Cl_{14} and is more soluble in $SiCl_4$ would be consistent with a more symmetrical structure. The possibility that this compound is the neopentasilane is suggested.

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The synthesis of N,N-difluorourea

(*Received* 13 *October* 1960)

WHEN urea is subjected to fluorine, diluted with nitrogen (ca. 1:5 to 1:10) in a flow reactor at 0°, a complex yellow, corrosive liquid containing up to 20 per cent active fluorine (to HI) and about 45–55 per cent total fluorine is obtained. Among the gaseous products obtained from the distillation of this

TABLE 1.—INFRA-RED SPECTRUM OF UNSYMMETRICAL DIFLUOROUREA

Dilute soln (cm^{-1})	Solid state (cm^{-1}) (Nujol mull)	Intensity	Assignment
3520		*m*	N—H stretch (free)
	3425	*m*	N—H stretch (bonded)
3420		*m*	N—H stretch (free)
	3320	*m*	N—H stretch (bonded)
3200	3200	*w*	—
2940	—	*w*	—
1803	1790	*s*	Amide I
1592	1613	*m*	Amide II
1345	1343	*m*	—
1115	1118	*w*	—
1018	1020	*m*	—
925	925	*m*	N—F (tentative)
892	—	*w*	—
836	836	*w*	—

corrosive liquid was difluoramine as previously reported by LAWTON and WEBER.[1] However distillation of the liquid also yields a solid sublimate and a solid or solid-liquid pot residue. These solid products were shown to have oxidizing power by reaction with hydriodic acid, and the oxidizing solid species are soluble in water, dichloromethane, and tetrahydrofuran, but slightly soluble in diethylether. Extraction with either dichloromethane or tetrahydrofuran, and evaporation of the resulting solutions yields crude difluorourea. The difluorourea may be purified by sublimation to form long thin needles melting at 41·0°–41·5°.

The solid was identified as unsymmetrical difluorourea by infra-red analysis and the structure was confirmed by wet chemical analysis. Infra-red spectra were obtained in dilute dichloromethane solution and in the solid phase as a mineral oil mull. All spectra were obtained on a Beckman IR-7 infra-red spectrophotometer. In dilute solution in non-polar solvents, primary amides give two absorption bands in the region 3500–3300 cm^{-1}. The first of these bands corresponds to the asymmetric stretching mode and is generally found around 3500 cm^{-1}. The second band, arising from the corresponding symmetrical mode, occurs around 3300 cm^{-1}. In dilute solution secondary amides

[1] E. A. LAWTON and J. Q. WEBER, *J. Amer. Chem. Soc.* **81**, 4755 (1959).

give rise to a single absorption in the range of 3460–3420 cm^{-1}. Unsymmetrical difluorourea has two strong bands at 3520 and 3420 cm^{-1} respectively, indicating the presence of an NH_2 grouping.

The bands at 1803 cm^{-1} and 1592 cm^{-1} in dilute solution in a non-polar solvent have been assigned as the Amide I and Amide II bands of an amide, respectively. The assignment of these bands was confirmed by the shift of these bands in the solid state spectrum. The Amide I band shifted from 1803 cm^{-1} in solution to 1790 cm^{-1} in the solid state while the Amide II band shifted from 1592 cm^{-1} in

TABLE 2.—SUMMARY OF WET CHEMICAL ANALYSES

Sought	Found	Calc
Active fluorine	38	39·6
Total fluorine	38·6	39·6
Total nitrogen	29·3	29·2
Amino nitrogen (NH_2)	14·6	14·6

dilute solution to 1613 cm^{-1} in the solid state. The direction of the shifts is in keeping with the proposed structure.[2] The large frequency shift of the Amide I band from a nominal 1700 cm^{-1} to 1803 cm^{-1} in dilute solution in a non-polar solvent indicates the presence of a strong electronegative group such as NF_2 attached directly to the $CO—NH_2$ structure. Accordingly, from the infra-red spectra, the chemical structure was confirmed as that of a primary amide.

The infra-red structural interpretation was confirmed by wet chemical analysis. Total fluorine was determined by the lead chlorofluoride titration,[3] while active fluorine was determined by reaction with potassium iodide and titration of the iodine liberated. Standard Kjeldahl techniques for nitrogen yielded one half of the theoretical nitrogen content because of the reaction of the $—HF_2$ group in acid to yield volatile difluoramine. Prior reduction of the $—NF_2$ group with HI yielded the theoretical nitrogen values. Accordingly, it was possible to differentiate between the NH_2 and NF_2 groups and confirm the unsymmetrical structure. The results of these analyses are shown in Table 2.

These data unambiguously identify the compound as unsymmetrical difluorourea, F_2NCONH_2. The hygroscopic compound may be stored in polyethylene but decomposes exothermically on being suddenly heated. The compound is a lachrymator and strong vesicant.

The authors are indebted to the Office of Naval Research for support of this work.

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[2] L. G. BELLAMY, *The Infrared Spectra of Complex Molecules*, (2nd Ed.) pp. 203–23. John Wiley, New York (1958).
[3] I. M. KOLTHOFF and J. J. LINGANE, *Polarography* (2nd Ed.) Vol. II. pp. 921–22, Interscience, New York (1952).

Preparation of long-lived hafnium-182*

(*Received* 25 *October* 1960)

IN a continuation of our programme[1,2] to investigate long-lived isotopes in the rare-earth region, a successful search for hafnium-182, produced by high flux neutron irradiation of hafnium-180, has been undertaken. For tantalum-182, the product of the β-decay of even–even hafnium-182, ground-state spins of 3 or 4 and odd parity are suggested by the coupling rule for odd–odd deformed core nuclei;[3]

* This work was performed under the auspices of the U.S. Atomic Energy Commission.

[1] R. A. NAUMANN, M. C. MICHEL and J. L. POWER, *J. Inorg. Nucl. Chem.* **15**, 195 (1960).
[2] R. A. NAUMANN, M. C. MICHEL and J. L. POWER, *J. Inorg. Nucl. Chem.* To be published.
[3] A. BOHR and B. R. MOTTELSON, *Kgl. Danske Videnskab. Selskab, Mat. -fys. Medd.* **27**, No. 16 (1953)
[4] P. AXEL. Private communication.

these spins are consistent with the decay scheme proposed for this isotope. A recent investigation[4] of the decay of the 16 min tantalum-182 isomer shows that the lowest lying excited states of tantalum-182 at 147 and 319 keV also have the same parity as that of the ground state but reveals higher spins. These observations, together with the near beta-stability of hafnium-182 predicted by semi-empirical mass formulae,[5] indicate that a low energy β-decay process, at least third forbidden, probably accounts for the non-occurrence of this nuclide in nature.[6]

During 1957, samples of hafnium were irradiated for six months in the Materials Testing Reactor at a neutron flux of 3×10^{14} neutrons/cm^2 per sec. These samples were contained in quartz ampoules and consisted of 10 mg of normal hafnium dioxide and 16 mg of hafnium dioxide enriched to 93·3 per cent in the mass 180 isotope. After irradiation, the samples were allowed to decay for thirty months before further examination. After this interval, the contents of the ampoules were dissolved in hydrofluoric acid and the solutions adjusted to concentrations of 12 N in sulfuric acid and 0·4 N in hydrofluoric acid. Successive extractions of these solutions with methyl-isobutyl ketone were carried out until scintillation spectra of the organic fractions taken with a deep well crystal revealed no tantalum-182 activity.

The isotopic composition of the hafnium remaining in the aqueous solution of the enriched sample was investigated by means of a 30 cm radius solid sample mass spectrometer equipped with an electron multiplier detector. The mass spectrum showed the presence of an isotope of mass 182. To confirm that the latter was indeed an isotope of hafnium, a portion of the enriched hafnium was subjected to a further chemical purification. An aliquot of the solution was evaporated in a platinum crucible which was flamed to remove sulphuric acid and sulphates. The residue was redissolved in a minimum of hydrofluoric acid and barium fluohafniate precipitated by the addition of barium nitrate. The barium compound, after washing, was redissolved in dilute nitric acid, containing boric acid, and hafnium precipitated as the hydrous oxide with ammonium hydroxide. After washing, the precipitate was redissolved in dilute nitric acid and reprecipitated with ammonium hydroxide. The mass spectrum of this repurified hafnium remained unchanged and showed the isotopic composition:

$$180 = 95{\cdot}02 \pm 0{\cdot}5\%$$
$$182 = 0{\cdot}072 \pm 0{\cdot}0036\%$$

These data were obtained by automatically scanning and recording the ion multiplier counting rate at the various mass positions until sufficient precision was obtained. The ratio of the mass 182 to mass 180 position appeared constant over a wide range of source conditions, further confirming the elemental identity of the ions recorded at these two positions. The background correction at the 182 mass position was made by averaging the readings at the 181 and 183 mass positions and at no time exceeded 10 per cent.

To search for evidence of decay of the hafnium-182, the remaining hafnium fraction was re-extracted with methyl isobutyl ketone 290 days after the initial extraction of tantalum. Tantalum-182 was positively identified in the scintillation spectrum of the organic fraction by the observation of the 100, 152, 220 and 1100–1200 keV γ-ray groups. From the counting rate of the tantalum-182 daughter we compute a saturation specific activity of 360 ± 180 dis/min per mg for the enriched sample of hafnium. This value together with the measured isotopic composition of this sample permits the calculation of a half-life of $8 \pm 5 \times 10^6$ years for hafnium-182. The radiations accompanying the decay of this isotope will be further investigated.

We wish to thank Dr. M. LINDNER of the Livermore Laboratory for communicating the results of his study of hafnium-182. The co-operation of the staff of the Materials Testing Reactor in providing this irradiation is gratefully acknowledged.

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[5] N. METROPOLIS and G. REITWEISNER, Document NP 1980, U.S. Atomic Energy Commission; H. B. LEVY, Document AECL 339, Atomic Energy Canada Ltd.; A. G. W. CAMERON, Document AECL 433, Atomic Energy Canada Ltd.

[6] F. A. WHITE, T. L. COLLINS and F. M. ROURKE, *Phys. Rev.* **101**, 1786 (1956).

Photo-annealing of (n,γ) effects in bromates

(*Received* 12 *October* 1960)

So far only two cases of photo-annealing of the effects of radiative thermal neutron capture have been reported.[1,2] In the case of potassium chromate a search for photo-annealing gave negative results[3] but this may have been due to a very high absorption coefficient of the chromate for the incident radiation, limiting the effect to a superficial layer of the crystals. The photo-annealing in irradiated phosphate proves to be a complicated reaction.[4]

An apparently simpler case of photo-annealing arises with calcium bromate. The thermal and radiation annealing of this material have been described elsewhere,[5] and the same analytical procedure as that previously described was employed in this study. Results obtained illuminating previously neutron irradiated anhydrous calcium bromate with the light from a Hanovia U.V.S. 250 lamp are recorded in Fig. 1. A duplicate of the experiment on the powdered material for the longest period of

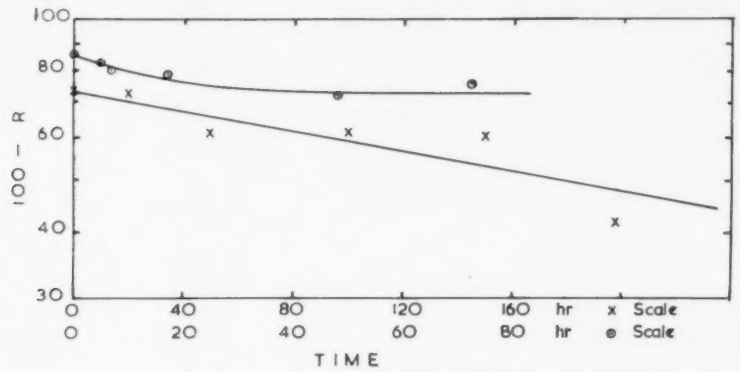

Fig. 1.

illumination but with a sheet of paper interposed between the lamp and the crystals, gave a retention, R, substantially the same as the unilluminated material. The crosses show the data for finely powdered calcium bromate, the circles refer to macrocrystalline material. The apparently limited change in the latter case may also reflect a high absorption coefficient of the crystals for the incident light. In the powdered samples an effectively larger volume of calcium bromate lies within a given distance from the surface of the crystals.

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Colour changes on heating copper(I) chloride

(*Received* 9 *November* 1960)

During the purification by vacuum distillation of copper(I) chloride, required for the measurement of its vapour pressure, striking changes in colour were observed which do not appear to have been

previously reported. The white solid obtained by the sulphur dioxide reduction of a hydrochloric acid solution of copper(II) chloride was filtered, washed and dried in a vacuum desiccator to give a product which possessed a greenish-blue tinge. This was mixed with a little copper powder and distilled under continuous evacuation using a two-stage rotary pump at about 500°C.

On repeated distillation, now in the absence of copper powder, it was seen that the white solid changed in colour to a deep blue at a temperature subsequently measured as 178 ± 3°C. The blue colour deepened as the temperature increased and just before melting, the now blue-black solid appeared to change in colour to green-black, and finally melted to give a deep-green coloured liquid. On cooling the melt the reverse sequence of colour changes was observed. The vapour condensed to a blue-black solid which changed back to white on cooling. The green-black to blue-black colour change was not seen in condensate, due most likely to the condensation taking place at a temperature much lower than that at which the colour change appeared in the heating sequence. These changes were consistently observed with several samples of the compound, which were found to be spectrographically free from other metals.

Of the univalent halides possessing the zinc blende structure, the properties of copper(I) chloride seem to have received the least attention and is the only one for which no phase transition is recorded. The colour changes described above may be indicative of such transitions.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, p. 193. Pergamon Press Ltd.

BOOK REVIEWS

VOL. 17 1961

H. J. EMELÉUS and A. G. SHARPE (Editors): **Advances in Inorganic Chemistry and Radiochemistry** Vol. 2. Academic Press, New York, 1960. viii + 392 pp., 86s.

THE second volume of *Advances* contains eight authoritative review articles by well known experts in their respective fields and continues the high quality set by the first volume of this series. There is in this volume rather a heavy bias towards sulphur chemistry with reviews by CADY on fluorine-containing sulphur compounds, by BECKE-GOEHRING on amides and imides of the oxyacids of sulphur, and by Foss on the structures of compounds containing chains of sulphur atoms. These articles jointly cover a wide range of sulphur chemistry and with the copious literature references provide very timely survey; the reviewer was particularly interested in the review by Foss, which contains references to his own extensive work in this area.

The first article, on stereochemistry of ionic solids by DUNITZ and ORGEL, provides a most useful collection of data on ionic solids and a brief account of the influence of crystal fields on transition metal stereochemistry with particular emphasis on distortions attributable to the Jahn-Teller effect.

EISCH and GILMAN report on organometallic compounds in a rather general way, and their article is by no means as exhaustive or well referenced as some of the others; they deal with new preparative techniques, structure, bonding and reactivities, and the discussion is concerned with what one can call classical metal–carbon bonds.

The solid halides of the actinide elements are well reviewed by KATZ and SHEFT and developments since KATZ and SEABORG'S *Chemistry of the Actinide Elements* are discussed; there is a wealth of structural, spectroscopic and thermodynamic information in the tables.

There is a rather brief but useful account of the chemical reactivity of the boron hydrides and related compounds by STONE, and finally an account of the use of mass spectrometry in nuclear chemistry by THODE, MCMULLEN and FRITZE which deals mainly with determinations of half-life, neutron-capture cross-sections and fission yields.

Annual review volumes of this type always suffer from the inherent disadvantage that only a few of the articles may be of interest to individual purchasers, and the joining of radiochemistry—which has little relevance to or overlap with inorganic chemistry—exacerbates this, but nevertheless the present volume can be strongly recommended for libraries.

G. WILKINSON

NUCLEAR SCIENCE SERIES—REPORT NUMBER 27: **Source Material for Radiochemistry.** National Academy of Sciences, Washington, D.C., 1959. 23 pp.

THIS pamphlet is a collection of very short abstracts. The underlying reason for its publication is a good one. A great deal of modern radiochemistry has been and is carried out in government controlled atomic energy establishments. The work is often published as reports which do not necessarily appear in the recognized scientific literature, although they are available to the general public if it knows where to apply. The main theme is the analysis of mixtures of radioisotopes, such as the fission products, and the majority of the papers are reviews of radiochemical methods, although several papers on counting techniques, decay schemes, tables of radioisotopes have been included. The papers are not exclusively official reports as many normal literature references are included, but when they are, the price and where to apply for them is given. The collection could be a useful starting point for information on analytical data of modern radiochemistry (although in this case I prefer to call it nuclear chemistry), but it should be emphasized, as the editors have done, that the collection is not exhaustive by any means and does not include, for instance, references to classical radiochemistry.

G. B. COOK

J. Inorg. Nucl. Chem., 1961, Vol. 17, p. 194. Pergamon Press Ltd.

ERRATUM

F. D. S. BUTEMENT and G. G. J. BOSWELL, New neutron deficient isotopes of krypton, *J. Inorg. Nucl. Chem.* **16,** 10–15 (1960).

Page 11, line 3 of 'Results' paragraph; for '21 min' read '12 min'.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 195 to 205. Pergamon Press Ltd. Printed in Northern Ireland

RADIOCHEMICAL STUDIES OF FISSION PRODUCT LANTHANUM AND LANTHANIDES—II

FISSION OF URANIUM INDUCED BY 170 MeV PROTONS*

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(*Received* 14 *July* 1960; *in revised form* 3 *October* 1960)

VOL. 17 1961

Abstract—The fission yields of isotopes of lanthanum and lanthanides have been measured in fission of natural uranium induced by 170 MeV protons. The measured cumulative yields of thirteen nuclides and independent yields of five nuclides are given. These yields have been used to evaluate the charge distribution in the mass region studied. The experimental data seem to give better support to the equal-charge-displacement than to the unchanged-charge-distribution hypothesis, but not decisively. The apparent fissioning nuclide is found to have a low mass number, about 230.

A survey of the widths of charge distribution curves for symmetric and asymmetric division with energy suggests that symmetric and asymmetric fission modes are different reactions and should be considered separately in any treatment of fission phenomena.

IN the previous paper (I) of this series an improved radiochemical method for the measurement of the yields of the lanthanides has been developed on the basis of a study of the carrying properties of lanthanum. The group isolation of the lanthanides from the fission product mixture is based on the use of lanthanum as a non-isotopic carrier. It is found to carry trace lanthanum and lanthanides satisfactorily in fluoride and hydroxide precipitations, a necessary requirement for the determination of the recovery yields of these elements at the end of the isolation procedure. The isolated lanthanides are separated from each other in a carrier-free state by cation-exchange chromatography using a small column and ammonium lactate as eluant. This method has many advantages compared to previous ones, as discussed in reference (1). For the present paper it is sufficient to emphasize that the time required for the whole procedure is only about one tenth of that used in earlier methods, thus allowing fission yield measurements even of short-lived nuclides to be made with a high degree of reliability.

This method has been applied to the determination of the yields of fission product lanthanum and lanthanides in the fission of uranium induced by 170 MeV protons, in order to gain more information about the mechanism of nuclear fission induced by high energy particles. Previous work on fission at the same energy carried out by the Oslo-Uppsala group is described in the papers by KJELBERG and PAPPAS[2] and by AAGAARD *et al.*[3]

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‡ Corrected in accordance with footnote (*) above.

[1] J. ALSTEAD and A. C. PAPPAS, *J. Inorg. Nucl. Chem.* **15** 222 (1960).
[2] A. KJELBERG and A. C. PAPPAS, *Nucl. Phys.* **1**, 322 (1956).
[3] P. AAGAARD, G. ANDERSSON, J. O. BURGMAN and A. C. PAPPAS, *J. Inorg. Nucl. Chem.* **5**, 105 (1957).

In these papers it is shown that 170 MeV proton induced fission in natural uranium results in the well known single peaked yield mass distribution curve giving a total fission cross section of about 1·6 ± 0·3 barns.*

In the region of the isotopes of iodine situated at the right shoulder of the yield mass curve the observed charge distribution curve has a surprisingly large width† at half-maximum of about four charge units.

In view of these findings it is of interest to seek more detailed insight into the mass and charge distribution at the wings of the yield mass curve. In the present paper, properties of the heavy wing are being studied while a study of the light wing is now in progress.[5]

I. EXPERIMENTAL

Treatment of target

The uranium target was the same uranium trioxide as used in the earlier investigations.[2,3] About 0·75 g of this was filled into small cylinders of 0·01 mm aluminium foil and irradiated with 170 MeV protons in the internal beam of the Uppsala synchrocyclotron. After an irradiation lasting one hour the target was dissolved in 3–5 ml 2 M nitric acid containing 1·00 mg of lanthanum and 2·00 mg of strontium carriers, both as nitrates. Lanthanum fluoride was precipitated from this solution, and lanthanum and lanthanides treated as described in reference (1). The final samples were all counted with Geiger–Mueller TGC-2 counters using mounting and counting techniques as previously described.[1]

Fission monitors

The 50·5 day ^{89}Sr was isolated from the supernatant liquid after the lanthanum fluoride precipitation and used as an internal fission monitor. The use of only 2·00 mg of carrier instead of the usual 20 mg is due to the requirement of obtaining as nearly as possible the same counting conditions for the monitor, lanthanum and the lanthanides. The standard chemical procedure given by GLENDENIN[6] for isolation of strontium in thermal fission, and frequently used in high energy fission studies, results in impure samples due to the entirely different distribution of products in these two processes. Therefore additional scavenging steps should be introduced[2]. The strontium was finally dissolved in 0·70 ml dilute nitric acid (monitor solution).

From this solution 0·050 ml volumes were withdrawn on strips of aluminum foil, dried and mounted for absolute counting. The samples were then essentially weightless and the self-absorption and self-scattering effects were very low. Volumes of 0·500 ml taken from the monitor solution were analysed for chemical yield using the microgravimetric method described by STREBINGER and MANDL[7].

The absolute fission yield of ^{89}Sr in the 170 MeV-proton-induced fission of uranium has been measured by KJELBERG and PAPPAS[2] as 31 ± 2 mbarns.‡

From the elution curve of the elements in the lanthanum series, relative fission yields of the respective nuclides concerned, i.e. isotopes of lanthanum to terbium inclusive, could be easily obtained provided a suitable internal lanthanide monitor was used. The 11·14 day ^{147}Nd was chosen as internal monitor, after first having been normalized to the 50·5 day ^{89}Sr. From its position in the series, the fission yield of ^{147}Nd is expected to represent a medium value.

The 11·14 day ^{147}Nd was isolated at the earliest one day after the end of the irradiation, when the shorter lived isotopes of neodymium, the 15 min ^{151}Nd (giving 27·5 hr ^{151}Pm) and the 2·0 hr ^{149}Nd (giving 54 hr ^{149}Pm) had decayed away.

* In reference (2) a value of 1·9 barn is given. Since then the cross-section of the reaction ^{27}Al (*p*, 3*pn*) ^{24}Na which forms the basis for the normalisation has been improved and lowered with about 20 per cent.[4]

† Throughout this paper the experimental distribution (not always pure Gaussian) is used and the widths of the curves are always measured at half-maximum of the distribution curve.

‡ Corrected in accordance with footnote (*) above.

[4] H. G. HICKS, P. C. STEVENSON and W. E. NERVIK, *Phys. Rev.* **102,** 1390 (1956).
[5] E. HAGEBØ and A. C. PAPPAS, To be published.
[6] L. E. GLENDENIN, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES. Plutonium Project Record, Div. IV, Vol. 9, Paper 236, McGraw-Hill New York (1951).
[7] R. STREBINGER and J. MANDL, *Michrochemie* **4,** 168 (1926).

The influence of the growth of the daughter, 2·64 year ^{147}Pm, in the decay curve of ^{147}Nd can be estimated using standard parent–daughter equations and taking into consideration the low counting efficiency of ^{147}Pm relative to that of ^{147}Nd, about 50 per cent. The maximum activity of ^{147}Pm is reached after about 2·5 months of decay and is then only about 0·5 per cent of the activity of ^{147}Nd at the time of separation. Thus the influence of the ^{147}Pm in the first part of the ^{147}Nd decay curve is considered to be negligible (Fig. 1).

The fission yield of ^{147}Nd is calculated from the measured data taking into consideration the low energy electrons from the 0·091 MeV converted gamma. This gives an absolute fission yield of ^{147}Nd of 8·1 ± 0·8 mbarns.

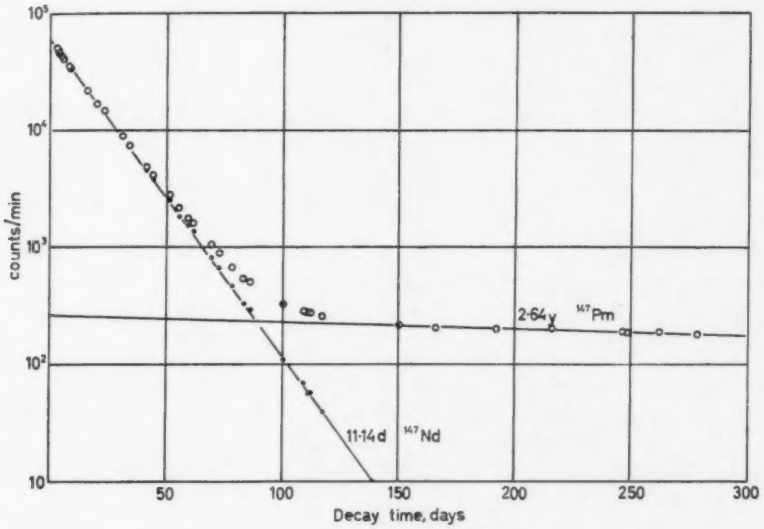

FIG. 1.—Decay of ^{147}Nd.

II. RESULTS

Cumulative fission yields of thirteen nuclides in the mass region 140 through 164 are given in Table 1. In Table 2 are given the results of some measurements of primary fission yields for five nuclides shielded by stable or long lived isobars having nuclear charges one unit lower. These results are the means of two or more independent measurements performed as described in the previous paper.[1]

The reliability in the determinations relative to the ^{89}Sr fission monitor is estimated as follows: The precision is according to the previous paper[1] 2–7 per cent. When errors due to the unavoidable variations in the proton beam, and to impurities in the target material,* as well as errors caused by uncertainties in counting corrections and half-lives are considered, then the relative yields are estimated to be reliable to 10–15 per cent.

When total cross-sections are of interest, the relative yields must be considered in the light of the standardisation of the fission monitor, 50·5 day ^{89}Sr. Using the value 31 ± 2 mbarns, the relative yields in column 2 have been recalculated to absolute

* A spectrographic analysis of the uranium trioxide proved the absence of lanthanides and could only detect lead as a fissionable element impurity. The amount found was 0·01 per cent. From the ratio of the fission cross sections involved the contribution to the fission products from lead was estimated not to exceed 10^{-3} per cent.

yields in column three in Table 1. These values are estimated to be reliable to about 15 per cent.

When considering the independent yields in Table 2, additional uncertainties should be taken into account due to lower yields and to the parent correction factors involved. We therefore estimate these data to possess a reliability of 20–30 per cent.

TABLE 1.—CUMULATIVE YIELDS OF LANTHANUM AND LANTHANIDE NUCLIDES IN 170 MeV PROTON INDUCED FISSION OF URANIUM*

Nuclide	Yield relative to ^{89}Sr	Absolute yield (mbarns)
^{141}La	0·66	20·4
^{143}Ce	0·50	16·0
^{145}Pr	0·39	12·0
^{147}Nd	0·26	8·1
^{149}Pm	0·17	5·4
^{151}Pm	0·09	2·8
^{153}Sm	0·055	1·7
^{156}Sm	0·015	0·47
^{157}Eu	0·016	0·50
^{159}Gd	0·014	0·45
^{161}Tb	0·0086	0·27
^{163}Tb	0·0034	0·11
^{164}Tb	0·0016	0·05

TABLE 2.—PRIMARY YIELDS OF LANTHANUM AND LANTHANIDE NUCLIDES IN 170 MeV PROTON INDUCED FISSION OF URANIUM*

Nuclide	Yield relative to ^{89}Sr	Absolute yield (mbarns)
^{140}La	0·16	5
^{142}Pr	0·05	1·6
^{143}Pr†	0·05	1·6
^{150}Pm	0·36	1·1
^{156}Eu	0·012	0·36

* The low energy conversion electrons occurring in the decay of some of these nuclides are taken into consideration through extrapolation of the β-components of an absorption curve in aluminium.

† The observed independent yield (equation 7 in reference (1)) of ^{143}Pr is a function of growth from ^{143}Ce as found by measurements at different growth times. A plot of the logarithm of the observed independent yield versus growth time is therefore used to determine the true independent yield.

III. DISCUSSION

Nuclear reactions at high energies (>100 MeV) start with the cascade process as described by SERBER[8] leaving residual nuclei with a broad excitation energy spectrum. In the following slower stage of the reaction de-excitation by nucleon evaporation (mostly neutrons) will compete with fission at any time. Thus the nuclides undergoing fission will cover a broad mass spectrum.

The most probable primary fission products must necessarily be closer to stability (Z_A) than in low energy induced fission, where the average fission product chains

[8] R. SERBER, *Phys. Rev.* **72**, 1114 (1947).

are 3–4 charge units and more than 99 per cent of the total chain yield is reached about 1–2 units below stability.[9]

In high energy induced fission, however, one might expect some contribution to the total chain yield from independent formation of stable nuclides. The magnitude of this will mainly depend on the extent of the cascade reactions, the spectrum of the excitation energy in the residual nuclei, the width of the charge distribution curve and the mass and energy dependence of the latter. Our knowledge is in this respect very scanty, but values for the width of the charge distribution curve in high energy induced fission of uranium ranging from about two to about four charge units are reported.[3,10–14]

The mass dependence of the observed width is not clear for high energy induced fission. In thermal and low energy induced fission, however, the measured width of the (non-Gaussian) charge distribution curve is 2·2 charge units,[9] and a single mass independent curve was first assumed and later experimentally verified.[9,15]* The same assumption concerning the mass dependence is often found in studies of high energy induced fission. However, this is scarcely justified due to lack of supporting experimental data.

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In fission studies there are only two assumptions which have proved successful in estimating the most probable primary charge. These are the unchanged charge distribution (UCD) and the equal charge displacement (ECD) mechanism.

The former is based on the assumption of a constant neutron to proton ratio (that of the fissioning nucleus) in the most probable primary fission fragment[16] and is ordinarily expected to be valid for high energy induced fission.[17]

According to this hypothesis the most probable primary charge Z_p is given by

$$Z_p = A \cdot \frac{Z_c - p}{A_c - n - p} \tag{1}$$

where A_c and Z_c are the mass and charge of the "compound nucleus" and n and p the average number of neutrons and protons emitted prior to fission.

The equal charge displacement hypothesis assumes equal chain lengths for the most probable complementary primary fragments[15] and is shown to be valid in thermal and low energy neutron induced fission.[9,15] Z_p is given by

$$Z_{p_1} = Z_{A_1} - \tfrac{1}{2}(Z_{A_1} + Z_{A_2} - Z_f) \tag{2}$$

* NOTE ADDED IN PROOF: According to A. C. WAHL (personal communication September 1960) the width is slightly mass dependent in thermal and low energy induced fission, when the charge distribution curves are assumed to be Gaussian. This observation, however, does not influence the conclusions drawn in the present paper.

[9] A. C. PAPPAS, *Proceeding of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, p. 19. United Nations, New York (1956).
[10] R. L. FOLGER, P. C. STEVENSON and G. T. SEABORG, *Phys. Rev.* **98**, 107 (1955).
[11] A. K. LAVRUKHINA and L. D. KRESAVINA, *J. Nucl. Energy* II, **5**, 236 (1957).
[12] F. I. PAVLOTSKAYA and A. K. LAVRUKHINA, *Soviet Phys.* **34**, (7), 732 (1958).
[13] B. D. PATE, J. S. FOSTER and L. YAFFE, *Canad. J. Chem.* **36**, 1691 (1958).
[14] A. P. VINOGRADOV, I. P. ALIMARIN, V. I. BARANOV, A. K. LAVRUKHINA, T. V. BARANOVA, F. I. PAVLOTSKAYA, A. A. BRAGINA and YU. V. YAKOVLEV, *Conference of the Academy of Sciences of the USSR on the Peaceful Uses of Atomic Energy*, Division of Chemical Science, p. 97, Moscow (1955); US-AEC-Translation p. 65, Washington (1956).
[15] L. E. GLENDENIN, C. D. CORYELL and R. R. EDWARDS, *Radiochemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMAN) NNES. Plutonium Project Record, Div. IV, Vol. 9, Paper 52. McGraw-Hill, New York (1951).
[16] N. SUGARMAN and T. TURKEVICH. Personal communication of 1946 in reference (15).
[17] R. H. GOECKERMAN and I. PERLMAN, *Phys. Rev.* **73**, 1127 (1948).

In thermal fission no neutron emission takes place prior to scission and one has assumed for simplicity the same number of neutrons emitted from both fragments A_1 and A_2, as the influence of the neutron distribution with fragment mass does not markedly alter the results due to the uncertainties inherent in Z_p from the values of Z_A.

Little is known about the actual time for the evaporation of neutrons in high energy induced fission. However, from measurements, of the angular distribution of neutrons emitted in the fission of natural uranium induced by 147 MeV protons HARDING and FARLEY[18] and SKYRME and HARDING[19] claim that the observed distribution is consistent with the emission of the majority of the neutrons before fission, while the number of neutrons emitted from the excited fission fragments seem to be the same as in thermal and low energy induced fission, i.e. on the average 2–3.

The yield-mass distribution

In accordance with this discussion one can not immediately consider the cumulative yields given in Table 1 as representing the total chain yields of the corresponding mass numbers. The nuclides in Table 1 represent the last or next to last member in the respective neutron rich fission-product decay chains. Depending on the values of the most probable primary charge and the width of the charge distribution curve, primary yields of stable or even neutron defficient nuclides may contribute to the total chain yield. In order therefore to get an idea to what extent the yields in Table 1 represent total chain yields, the results of Monte Carlo calculations of both the initial cascade and the subsequent evaporation process will be used.

From the curves given by METROPOLIS *et al.*[20] the nuclides present at the end of a cascade initiated in natural uranium by 155 MeV protons,* their frequencies and average excitation energies can be estimated. It is found that the nuclei terminating the cascade average around $Z = 92{\cdot}5$ and $A = 237{\cdot}7$ i.e. about 0·8 charge units on the neutron rich side of stability. The excitation energy shows a very broad distribution averaging about 87 MeV. This value is consistent with 88 ± 18 MeV as measured by GROSS[21].

Considering the low probability for proton evaporation,[22] ^{237}U should be a representative from which neutron evaporation starts.

The fate of this nucleus will depend on the neutron binding energies and the fission barriers involved, in other words on the type of nucleus and on the ratio of fission to neutron width. The lower extreme in A and Z of the fissioning nucleus is found by assuming de-excitation by evaporation only.

According to SKYRME and HARDING[19] the mean kinetic energy of the neutrons evaporated from uranium bombarded with 150 MeV protons is $2{\cdot}4 \pm 0{\cdot}2$ MeV. The average energy degradation by evaporation of a neutron should therefore be $B^n + 2{\cdot}4$ MeV, where B^n is the neutron binding energy.[23] The lowest mass which the uranium

* The maximum proton energy in the present investigation is 170 MeV but the maximum intensity is ~15 MeV below, thus ~155 MeV should be used in these calculations.

[18] G. N. HARDING and F. J. M. FARLEY, *Proc. Phys. Soc.* (London) **69** A 853 (1956).
[19] D. M. SKYRME and G. N. HARDING, *Nuovo Cimento* (X). **9**, 1082 (1958).
[20] M. METROPOLIS, R. BIVINS, M. STORM, A. TURKEVICH, J. M. MILLER and G. FRIEDLANDER, *Phys. Rev.* **110**, 185 (1958).
[21] E. E. GROSS, Report UCRL-3337 (1956).
[22] I. DOSTROVSKY, P. RABINOWITZ, R. BIVINS, *Phys. Rev.* **111**, 1659 (1958).
[23] A. G. W. CAMERON, Report AECL-433/CRP-690 (1957).

nucleus can possess after the evaporation process can thus be estimated to be 230. When fission of this nucleus takes place, two to three neutrons will be emitted from the fragments. It should be kept in mind, however, that one has a broad energy distribution at the end of the cascade process. Thus this estimate gives only average values.

The most probable fissioning nucleus may be of higher mass due to the high fission probability of the nuclides left after the evaporation of only a few nucleons, as these would have a favourable Z^2/A value. Fission may therefore take place to different

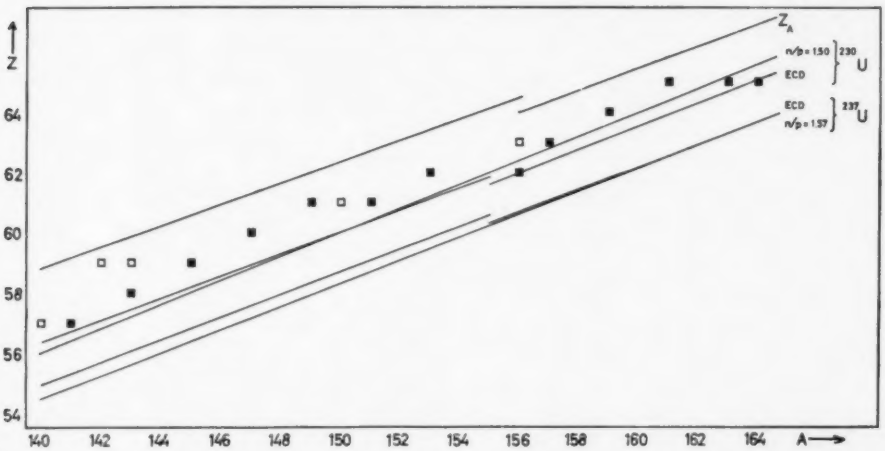

FIG. 2.—Positions of studied nuclides in relation to the nuclear stability curve (Z_A) and to the most probable primary charges. The latter are computed for ^{237}U and ^{230}U according to ECD and UCD hypotheses: ■ nuclides with measured cumulative yields; □ nuclides with measured independent yields.

degrees along the whole evaporation path, i.e. from ^{237}U to ^{230}U. The number of neutrons emitted from the fragments will depend on the excitation energy and will be correspondingly large if fission occur in highly excited nuclei. (The kinetic energy of the fission fragments depends only very little on the energy of the bombarding proton.[24]) The apparent fissioning nucleus obtained on the basis of the observed mass distribution will therefore always show a lower mass number than the actual one.

The nuclides given in Table 1 are plotted in Fig. 2 and are located at a reasonable distance from the Z_p curves, indicating that the measured cumulative yields must be close to total chain yields.

Using the yields in Table 1 and the two charge distribution hypothesis for the most unfavourable situation, ^{230}U the distribution curve obtained is given in Fig. 3, which proves that the majority of the measured values are good representations for chain yields, whichever approach is used.

The chain yields calculated from the measured cumulative yields show only small scattering and a smooth distribution for the heavy wing of the yield mass curve can be drawn. This is compatible with an exponential decrease of yields with increasing mass number. The slope of the wing, given as $d(\log y)/dA$, about $-0{\cdot}10$ reciprocal mass number, is in accordance with the general observation that the yield mass curve spreads out with increasing bombarding energy.[25]

[24] I. HALPERN, *Ann. Rev. Nucl. Sci.* **9**, 245 (1959).
[25] H. G. HICKS and R. S. GILBERT, *Phys. Rev.* **100**, 1286 (1955).

The charge distribution

The independent yields of the nuclides given in Table 2 are converted to fractional chain yields by dividing with the corresponding mass yields, taken from the curve in Fig. 3. The results are given in Table 3.

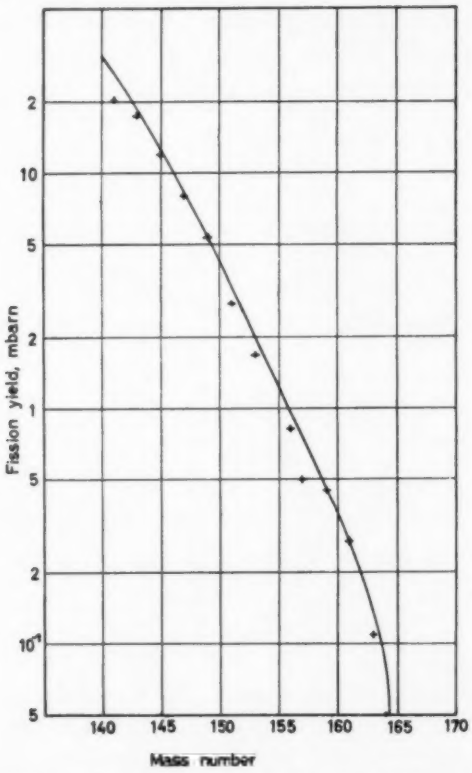

FIG. 3.—Part of yield-mass curve for 170 MeV proton induced fission in uranium. Solid line: calculated total chain yields as given in the text: + measured cumulative yields.

TABLE 3.—FRACTIONAL CHAIN YIELDS OF SHIELDED NUCLIDES

Nuclide	Fractional yield
^{140}La	0·16
^{142}Pr	0·064
^{143}Pr	0·084
^{150}Pm	0·27
^{156}Eu	0·37

In accordance with the previous discussions in this paper and due to our scant knowledge to details of the high energy induced fission processes, especially those modes responsible for the asymmetric part of the yield mass curve, the present authors have considered the determination of Z_p according to both equations (1) and (2), i.e. the UCD and ECD hypothesis, respectively. As a first approximation we assume

a constant shape and width of the charge distribution curves with mass in this limited region. In both cases calculations are performed for fissioning nuclei covering the mass region down to 230. In Figs. 4a and b the fractional yields are plotted as functions of the distance $Z - Z_p$ from the most probable primary charge, for unchanged charge distribution and equal charge displacement respectively. In Fig. 4c the broad charge

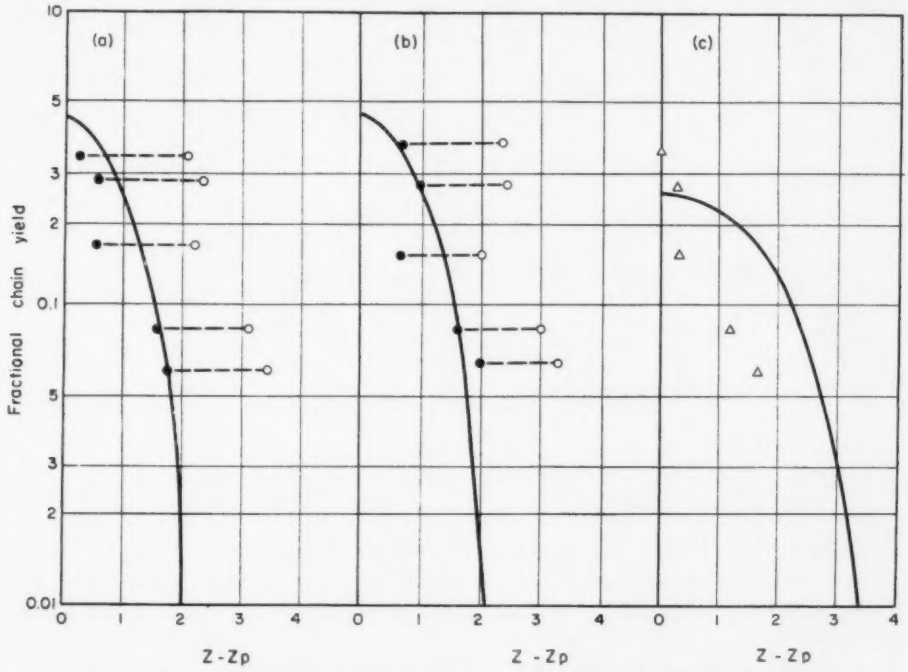

FIG. 4.—Charge distribution curves for the heavy wing of the yield mass curve in 170 MeV proton induced fission in uranium: ○ fissioning nuclide ^{237}U; ● fissioning nuclide ^{230}U.
a. Distribution on the basis of the UCD hypothesis, width 2·2 of the curve.
b. Distribution on the basis of the ECD hypothesis, width 2·2 of the curve.
c. Distribution on the basis of $n/p = 1{\cdot}49$ as found in the region of isotopes of iodine with width 4·0 of the curve.
(The uncertainties in the measured independent yields are discussed in the text.)

distribution found by AAGAARD *et al.*[3], based on the UCD hypothesis and valid in the region of the isotopes of iodine is given. The fractional yields are plotted using the n/p value found by these authors, 1·49.

These figures do not show decisively which mechanism governs the charge distribution in the mass region studied, but seem to favour rather the equal charge displacement rule (Fig. 4b). However, the measured fractional yields, in Fig. 4 point towards an 'apparent' fissioning nucleus with low mass and a narrow charge distribution curve with a width about the same as for thermal fission. This is considerably smaller than the 4·0 charge units determined by AAGAARD *et al.*[3] in the mass region of iodine.*

Such a large difference in the charge distribution curves for the symmetrical and the asymmetrical part of the mass distribution has not been clearly realized in earlier

* As this region is well above the shoulder of the yield mass curve and sufficiently close to symmetric division ($A \sim 115$–120) it should be considered as belonging to the central part of the mass distribution curve.

work, probably due to scarcity of data and to the methods used in the interpretation and presentation of the experimental values.

Studies of charge distribution curves closer to symmetric fission (isotopes of iodine and tellurium in thorium fission) by PATE *et al.*[13] show that the width increases with the energy of the bombarding particle. These data together with those in reference (3) and the present work suggest the feasibility of a study of the energy dependence of the charge distribution curves for symmetric and for asymmetric division modes separately.

In thermal and low energy induced fission the shape of the charge distribution curve

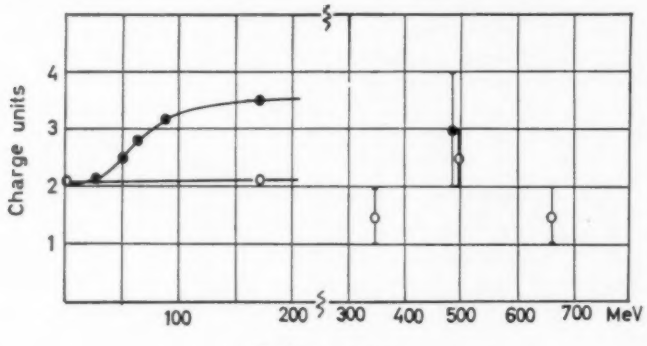

FIG. 5.—Width of charge distribution curves for symmetric and asymmetric fission mode as function of bombarding energy: ○ asymmetric division; ● symmetric division.

seems to be independent of the mass of the fission product chain.* This is also supported by the statistical treatment of the fission process given by FONG[26]. The ratio of asymmetric to symmetric divsion is, however, very high, in the low energy process about 600, making reliable measurements of independent fission yields very difficult for the symmetric mode, and none are really available. Fig. 5 supports the conclusions drawn from low energy fission studies that the widths of the charge distribution curves for symmetric and asymmetric division are about the same at low energies.

At energies above 25 MeV the observed width for the symmetric division starts departing from that of the asymmetric division. While the latter seems to remain constant with energy at about two charge units, the former increases with energy reaching a width of about four charge units at 200 MeV after which it seems to level off.

An estimate of the trend above the 200 MeV region has been made by trying to re-interpret the data in references (10)–(12) and (14) in the light of the results of the present investigation. The crude values obtained are included in Fig. 5 and are not inconsistent with reasonable extrapolations from the region below 200 MeV. Thus the difference in the widths seems to persist up to very high bombarding energies and the charge distribution curves may be used as an indication of the mode of fission responsible for the different parts of the mass distribution curve.

The knowledge that the charge distribution curve is narrow for a single fissioning nuclide at low energies might enable us to say that the competition between neutron evaporation and fission at high energy should result in a broader charge distribution

* See note added in proof p. 5.

[26] P. FONG, *Phys. Rev.* **102**, 434 (1956).

curve. This curve would be the sum of narrow curves (widths about 2·2 charge units), each corresponding to a fissioning nuclide with slightly different neutron to proton ratio. Thus the upper curve in Fig. 5 is explained in this way.

For a given irradiation energy one should, according to this general picture, immediately expect the width of the charge distribution curve to increase with the mass of the fission product chain, if the whole mass distribution at high energy bombardment is the result of one type of (symmetric) fission. This is, however, not borne out by the results of the present investigation, which shows that the width at high masses is small Therefore, a change in the interpretation of fission phenomena at high energies seems justified.

The observed effects can only be understood by considering the asymmetric fission and the symmetric fission as two distinct different types of fission. In high energy induced fission the asymmetric fission process is responsible for the heavy and light wing of the yield mass curve, while the middle part of the curve is due to the symmetric fission process. The symmetric mode, in contrast to the asymmetric mode, increases with increasing energy.[27] Furthermore, symmetric fission seems to be associated with an unchanged charge distribution[17] while we know that asymmetric fission is associated with equal charge displacement.[9] The present work is therefore not inconsistent with an idea of a mass dependent mixture of both charge distribution rules in high energy induced fission.

The two fission modes may after all be associated with quite different paths for the fissioning nucleus over the barrier on its way to scission, and the ratio determined entirely by the excitation energy available.

Acknowledgement—The authors are indebted to CERN Theoretical Study Division (Copenhagen) for fellowships granted in order to perform this study at the Gustaf Werners Institute for Nuclear Chemistry, Uppsala, Sweden. We also wish to express our thanks to the Director of the Institute, Professor T. SVEDBERG for his interest in this work and to the staff of the Uppsala synchrocyclotron for help during the bombardments.

[27] G. RUDSTAM and A. C. PAPPAS, *Nucl. Phys.* In press.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 206 to 209. Pergamon Press Ltd. Printed in Northern Ireland

THE YIELD RATIO OF THE ISOMERIC PAIR ^{197m,197}Hg FORMED BY ^{197}Au(d,2n)^{197}Hg REACTION

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(*Received* 12 *May* 1960; *in revised form* 5 *July* 1960)

Abstract—The yield ratio of the isomeric pair formed by the reaction ^{197}Au(d,2n) was measured at different deuteron energies between 9 and 26 MeV. The results are briefly discussed.

STUDIES of the yield ratios of isomeric pairs produced in nuclear reactions are of interest in determining the mechanism of formation of these isomers.

It was observed experimentally[1,2] that in different nuclear reactions where the same isomeric pair is produced, there is a variation in the ratio for the same excitation energy.

It was considered of some interest to study the yield ratio of the isomeric states ^{197m}Hg (spin $\frac{13}{2}+$) and ^{197}Hg (spin $\frac{1}{2}-$) in the nuclear reaction ^{197}Au(d,2n)^{197}Hg. Experiments were performed irradiating gold with deuterons of energies ranging from 9 to 26 MeV.

EXPERIMENTAL

The yield ratio of the isomeric pair ^{197m}Hg/^{197}Hg in the reaction Au(d,2n) was measured varying the deuteron energies between 9 and 26 MeV.

The yields of the isomeric pair were obtained using the stacked foil technique with 25 mg/cm^2 thick gold foils, which allowed simultaneous bombardment over a wide range of energies. The individual excitation functions of the isomers could not be determined absolutely owing to the flux variation across the gold foils.

The irradiations were performed using the internal beam of a 180 cm diameter synchrocyclotron in the orbit corresponding to 28·1 MeV energy. The variation of the radius of curvature inside the cyclotron over the width of absorber traversed by the particles was insignificant. The maximum dispersion of the beam was estimated to be 1·2 MeV at 28·1 MeV energy.

The deuteron energy in each foil of the stack was calculated from the range-energy curves of AARON *et al.*[3]

Separation methods

The irradiated foils were washed with dilute HCl and amalgamated with a small quantity of mercury. The mercury was separated from the gold by vacuum distillation at an elevated temperature. In this way the radioactive mercury was distilled with the carrier, and collected on inactive gold foils for later measurements.[4,5]

Measurements method

Figure 1 shows the disintegration scheme of the isomeric pair under consideration.[6]

[1] R. A. SHARP and A. C. PAPPAS, *J. Inorg. Nucl. Chem.* **10**, 173 (1959).
[2] K. I. ZHEREBTSOVA, T. P. MAKAROVA, Y. A. NEMILOV and B. L. FUNSTEIN, *Zh. Eksptl. Teoret. Fiz.* **35**, 1355 (1958).
[3] W. A. AARON, B. G. HOFFMAN and F. C. WILLIAMS, U.S.A.E.C. Report (UCRL 663 (1951).
[4] H. FRAUENFELDER, M. WALTER and W. ZUNTI, *Phys. Rev.* **77**, 557 (1950).
[5] D. L. HUFFORD and B. F. SCOTT, *Radio Chemical Studies: The Fission Products* (Edited by C. D. CORYELL and N. SUGARMON) NNES, Plutonium Project Record, Div. IV, Vol. 14B Paper 16, p. 1. McGraw-Hill, New York (1951).
[6] D. STROMINGER, J. M. HOLLANDER and G. T. SEABORG, *Revs. Modern Phys.* **30**, 777 (1958).

The relative yields of the isomers of 24 and 65 hr can be determined measuring the relative intensities of the 279 and 192 KeV γ-rays. Counting was performed with a single channel scintillation spectrometer[7] using a NaI(Tl) 1 × 1 in. crystal and an E.M.I. 6262 B. photomultiplier tube. To

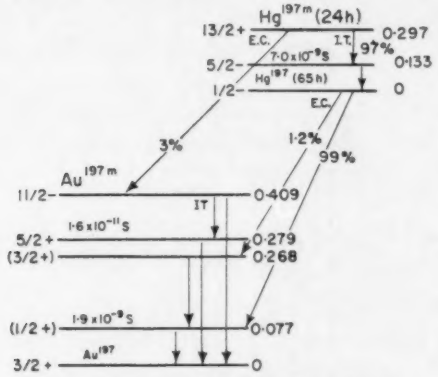

FIG. 1.—^{197m,197}Hg disintegration scheme.

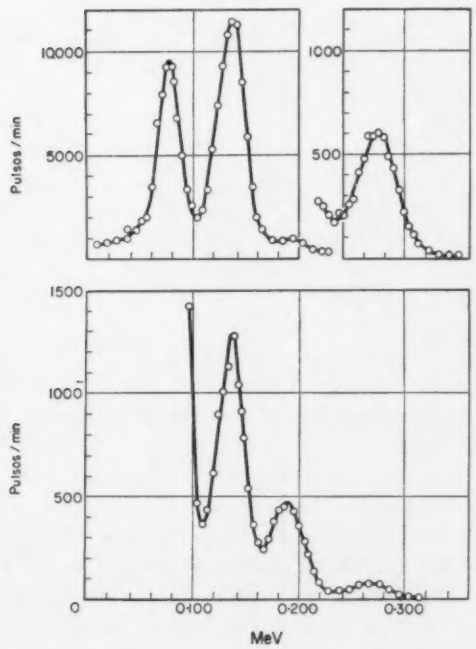

FIG. 2.—^{197m,197}Hg γ-spectrum at different times from the end of irradiation.

avoid pile-up effects a tin foil of 0·581 g/cm² and another of molybdenum of 0·153 g/cm² were used as absorbers and the same geometry was used in all the measurements.

Figure 2 shows as an example the ^{197}Hg spectra corresponding to 17·2 ± 0·2 MeV deuteron energy, at different times after the end of irradiation.

The areas under the 279 and 192 keV photopeaks were obtained by graphical integration. The usual counting corrections were made and the disintegration scheme was taken into account when

[7] K. FRANZ and S. F. PINASCO. *Publicaciones C.N.E.A. Serie Fisica.* Vol. 1, No. 13 (1957) Rep. Argentina.

calculating the photopeak at each deuteron energy. At irradiation energies greater than 18 MeV, ^{195}Hg is produced by ^{197}Au(d,4n) reaction. The subtraction of this nuclide introduces some errors in the determination of the photopeak areas.* The values of the ratio σ_m/σ_g at the different deuteron energies used are given in Table 1. The energy values shown are the average between the incident and the emergent deuteron energies.

Figure 3 shows the ratio σ_m/σ_g plotted against the energy of the incident particles.

TABLE 1.

Energy (MeV)	σ_m/σ_g
8·8 ± 0·5	0·21
11·1 ± 0·3	0·42
14·7 ± 0·3	1·15
17·9 ± 0·2	1·30
20·8 ± 0·3	1·45
23·5 ± 0·2	1·25
25·9 ± 0·2	1·25

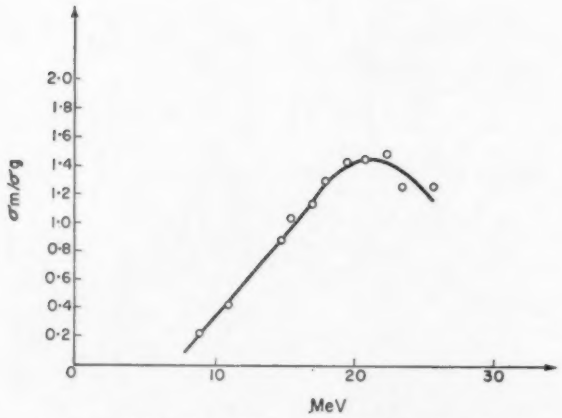

FIG. 3.—Yield ratio of ^{95}Nb isomers as a function of deuteron energy.

DISCUSSION

Several factors influence the yield ratio of the isomeric pairs in nuclear reactions and they have been discussed by different authors.[4,9,10]

With simple bombarding particles a detailed study of these effects leads to some theoretical predictions of the reaction mechanism producing the isomeric states. With deuteron irradiation complications arise, since in this case, different processes such as total absorption of the deuteron or stripping can take place. This fact makes all theoretical considerations difficult. Generally in nuclear reactions at 30 MeV or lower energy only the "compound nucleus" formation is considered. In this case at low excitation energies, the formation of the isomer with spin similar to that of the target nucleus would be favoured. An increase in the excitation energy introduces

* Above 22 MeV these errors could be roughly estimated at about ±15 per cent.

[8] J. K. MEADOWS, R. M. DIAMOND and R. A. SHARP *Phys. Rev.* **102,** 190 (1956).
[9] B. LINDER and R. A. JAMES, *Phys. Rev.* **114,** 322 (1959).
[10] S. M. BAILEY. U.S.A.E.C. Report UCRL, 8710 (1959).

other factors that would lead to an increase in the yield of the initially unfavourable isomeric state.

An examination of Fig. 3 shows that at low energies, the formation of ^{197}Hg with a spin of $\frac{1}{2}-$ is favoured. This isomer has a spin closer to that of the target nucleus, ^{197}Au, whose fundamental state is $\frac{3}{2}+$. The proportion of the isomer with spin $\frac{13}{2}+$, increases with increasing deuteron energy.

Therefore, it can be concluded that the function relating the yield ratio of the isomeric states with energy shows the general trend observed in other reactions.[2,8,9] The upper limit of available energies (28·1 MeV) and the increasing experimental errors (above 23 MeV the formation of ^{195}Hg increases), do not permit us to state whether the curve tends to a limiting value or whether it reaches a maximum at 20–22 MeV and then decreases.

Acknowledgements—The authors wish to express their appreciation to the C.N.E.A. syncrocyclotron group for the irradiations performed and to Miss E. MENDOZA for her help.

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J. Inorg. Nucl. Chem. 1961, Vol. 17, pp. 210 to 214. Pergamon Press Ltd. Printed in Northern Ireland

REACTOR-IRRADIATED PHOSPHORYL CHLORIDE[1]

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(*Received* 4 *July* 1960; *in revised form* 25 *October* 1960)

Abstract—Samples of $POCl_3$ were reactor irradiated for varying periods of time in a thermal neutron flux of approximately 6×10^{11} n cm^{-2} sec^{-1}. The irradiated samples were examined by carrier distillation techniques which showed the presence of $^{32}PCl_3$, $^{32}POCl_3$ and a labelled high-boiling component. A changing distribution of ^{32}P in the products was observed. The percentage of total ^{32}P found in combination as $^{32}PCl_3$ decreased from about 60 per cent to less than 10 per cent with increasing irradiation time while that found as $^{32}POCl_3$ increased from about 30 per cent to greater than 80 per cent. Phosphorus exchange in the system PCl_3–$^{32}POCl_3$ was investigated and appeared to be negligible for the distillation conditions used in this study.

THE distribution of ^{32}P-labelled products in reactor-irradiated phosphorus trichloride was found to be dependent upon the time of irradiation, and preliminary results indicated a similar effect in $POCl_3$.[3] The present study was undertaken to investigate further the relationship between exposure time and distribution of labelled products in reactor-irradiated $POCl_3$. Also it was desired to determine the mechanisms by which the products were formed, if possible.

EXPERIMENTAL

Reagents. All reagents except decane were purified by methods reported previously.[3] Decane (Matheson, Coleman and Bell 5845) was used as a high-boiling hold-back carrier after extensive purification to remove aromatic and unsaturated impurities. The UV absorption spectrum was observed with a Carey recording spectrophotometer. The impure decane was first treated by slow addition of a 1:3 conc HNO_3, conc H_2SO_4 solution with vigorous stirring after which the mixture was refluxed for 6–8 hr. The decane was separated, washed to remove excess acid and then dried over anhydrous $CaCl_2$. This was followed by repeated distillations from molten sodium to obtain the pure material.

Capsuling. $POCl_3$ (5–7 ml) was transferred by reduced pressure distillation into quartz capsules for irradiation. In two special samples small amounts of PCl_3 were added to the samples before sealing. This was done by crushing glass ampoules of PCl_3 in a side-arm connected to the system and transferring the contents by distillation into the quartz capsules containing phosphoryl chloride.

Irradiation. All reactor irradiations were done in hole 10 of the X-10 graphite-moderated reactor at the Oak Ridge National Laboratory. A thermal neutron flux of 6×10^{11} n cm^{-2} sec^{-1} was requested at which level the associated reactor γ-ray intensity[4] was about $1{\cdot}55 \times 10^6$ r hr^{-1}. Irradiation periods of 30 sec to 24 hr were used in the study. One special sample was given an additional irradiation with γ-rays from a high intensity cobalt-60 source at Oak Ridge National Laboratory. For each sample, approximately three days elapsed between removal from the reactor and analysis.

Separation. The samples were opened in an inert atmosphere of CO_2.[5] Carrier materials (PCl_3, $POCl_3$, $PSCl_3$, and decane) were added, aliquots were withdrawn for radioassay and the

[1] Based on the Ph.D. thesis of T. J. CLARK, Kansas State University, 1958. Work performed under U.S. A.E.C. Contract AT-(11-1)-584.
[2] Present address: Hanford Laboratories Operation, General Electric Company, Richland, Washington.
[3] D. W. SETSER, H. C. MOSER and R. E. HEIN, *J. Amer. Chem. Soc.* **81**, 4162 (1959).
[4] J. H. GILLETTE. Private communication.
[5] T. J. CLARK, P. K. CONN and R. E. HEIN, *Chem. Anal.* **44**, 55 (1955).

mixtures were distilled through a jacketed column which had 11·7 theoretical plates. The fractions were collected in calibrated receivers, about 5 to 10 fractions being collected for each carrier distilled.

Radioassay. Counting was done with a dipping tube assembly which had an efficiency of 10 per cent for ^{32}P but was insensitive to ^{35}S. ^{35}S was present in the samples from ^{35}Cl $(n, p)^{35}S$ reactions.

RESULTS

The results of radioassay for the various fractions of a typical sample (*K*, Table 1) are shown in Fig. 1. The constant specific activity of the fractions within the PCl_3 and

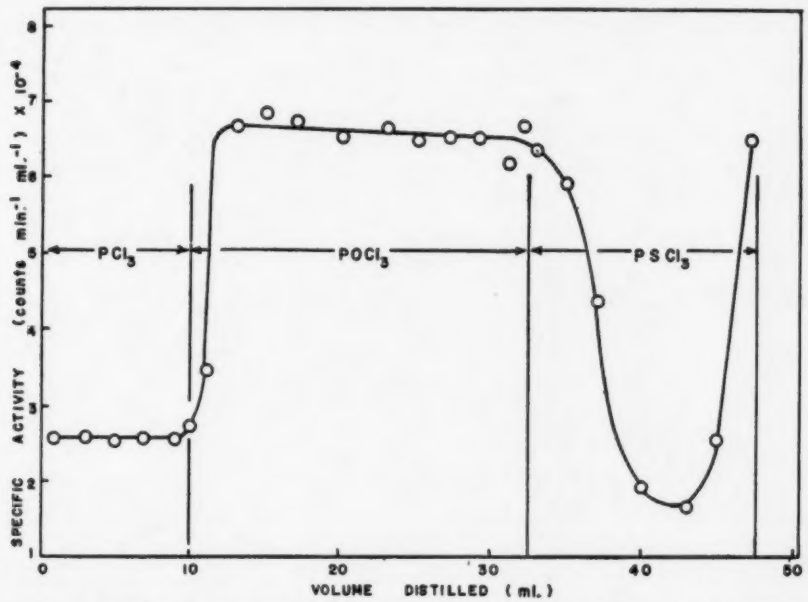

FIG. 1.—Specific activities of carrier fractions from the distillation of reactor-irradiated $POCl_3$.

$POCl_3$ components indicates that the ^{32}P was combined as $^{32}PCl_3$ and $^{32}POCl_3$ in these fractions.

Specific activity of the $PSCl_3$ fractions was not constant so the $PSCl_3$ fractions were re-combined, $POCl_3$ and decane carriers were added and the separation procedures were repeated. Most of the radioactivity was carried by the $POCl_3$ or retained in the decane. Some of the $PSCl_3$ fractions were essentially free of ^{32}P radioactivity. These results indicated that the radioactivity in the $PSCl_3$ fractions of sample *K* was mostly labelled $POCl_3$ and labelled high-boiling material.

The average specific activity was determined from the fractions collected for each component; this was multiplied by the volume of the carrier to determine the total radioactivity of the component. The total sample radioactivity was determined from aliquots removed before distillation and was used to calculate (with appropriate decay and counter efficiency corrections) the amount of ^{32}P present at the time of removal from the reactor. The results are given in Table 1 in order of increasing ^{32}P concentration, which is proportional to the neutron dosage received by each sample.

The possibility of exchange of phosphorus atoms between PCl_3 and $POCl_3$ was investigated since this exchange could lead to erroneous conclusions for distributions

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and mechanism. A mixture of 14 ml ^{32}P labelled $POCl_3$, 10 ml PCl_3 and 20 ml decane was separated under conditions similar to those used for reactor-irradiated samples. The PCl_3 fractions were not all of equal specific activity, and the total amount of activity in the PCl_3 was only 0·44 per cent of the total. It was concluded that phosphorus exchange between $POCl_3$ and PCl_3 was not important for the distillation conditions used in this study.

TABLE 1.—PERCENTAGE OF TOTAL ^{32}P IN VARIOUS COMPONENTS OF REACTOR-IRRADIATED $POCl_3$ SAMPLES

Sample	Requested irradiation time	^{32}P Concentration (atoms ml^{-1})	PCl_3 (%)	$POCl_3$ (%)	High-boiling component (%)
A	30 sec	$2·94 \times 10^9$	16	54	16
B	30 sec	$4·47 \times 10^9$	29	36	34
C	30 sec	$4·48 \times 10^9$	57	30	6
D	1 min	$7·69 \times 10^9$	63	34	7
E	1 min	$1·54 \times 10^{10}$	41	37	19
F	3 min	$2·51 \times 10^{10}$	43	43	9
G	4 min	$3·45 \times 10^{10}$	18	46	31
H	5 min	$5·23 \times 10^{10}$	11	67	18
I	5 min	$5·94 \times 10^{10}$	9	47	33
J	10 min	$8·69 \times 10^{10}$	15	62	22
K	10 min	$1·24 \times 10^{11}$	10	55	33
L	20 min	$2·13 \times 10^{11}$	9	55	36
M	20 min	$2·44 \times 10^{11}$	8	57	36
N	1 hr	$7·63 \times 10^{11}$	6	84	6
O	24 hr	$1·84 \times 10^{12}$	4	84	7
P[a]	30 sec	$5·12 \times 10^9$	1	35	61
Q[b]	1 min	$1·64 \times 10^{10}$	80	11	5
R[c]	4 min	$4·95 \times 10^{10}$	80	15	2

[a] This sample was subsequently irradiated with ^{60}Co γ-rays for 10 hr 54 min at an intensity of $2·2 \times 10^6$ r hr^{-1}.
[b] Sample *Q* contained 3·7 per cent by weight added PCl_3.
[c] Sample *R* contained 1·4 per cent by weight added PCl_3.

DISCUSSION

In general, the sum of the radioactivity recovered in the components was 95 per cent or more of the total ^{32}P for a given sample. In cases where less than 100 per cent was recovered the losses were attributed to errors in volume estimation, adsorption of activity on glass surfaces or counting sample preparation. In addition, some errors may have been involved in determining total component activity as the product of the average specific activity of the fractions of a component and the total volume of the component. In samples *D* and *M* the apparent recoveries were slightly greater than 100 per cent. No explanation can be offered, but it should be pointed out that the errors might compound to give such results.

The low percentage of ^{32}P in the PCl_3 fractions of samples *A* and *B* was probably due to loss by hydrolysis during distillation. Sample *C* was irradiated under similar conditions but distilled with more precautions to prevent such hydrolysis. The precautionary measures included additional flaming of the glass distillation equipment and a modification of the order of addition of carrier materials, in which PCl_3 was added to

the distillation flask and swirled before the sample and the other carriers were added.

Species containing ^{32}P. Both $^{32}PCl_3$ and $^{32}POCl_3$ were formed during reactor irradiation as evidenced by the fact that the PCl_3 fractions from each distillation had equal specific activities and the same was true for the $POCl_3$ fractions. The component designated as 'high-boiling material' (Table 1) was not identified but had some properties of PCl_5. It consistently distilled with the first part of the decane carrier (b.p. 174°). The material was readily extracted from decane in a water soluble form, but it appeared to resist chemical reduction by white phosphorus or powdered antimony.

The formation of $^{32}PCl_5$ seems plausible because the reactive portion of the environment of recoil fragments should be predominantly chlorine. Chlorine should be freed from both ionization–excitation and recoil processes. Considering the latter process alone, there would be approximately 360 times as many (n,γ) reactions in chlorine as in phosphorus.

Radiation effects. There is a marked radiation effect on the distribution of ^{32}P labelled products in reactor-irradiated $POCl_3$ as shown by the results given in Table 1. Distribution of ^{32}P in samples *N* and *O*, irradiated for the longest times, indicates that the formation of $^{32}POCl_3$ is ultimately favoured. Other irradiations gave prominent yields of additional species, and in samples *Q* and *R*, $^{32}PCl_3$ and $^{32}POCl_3$ appear as the principal primary products of the $^{31}P(n,\gamma)^{32}P$ reactions. Secondary radiation-induced reactions evidently convert part of the $^{32}PCl_3$ into $^{32}POCl_3$ and labelled high 'boiling component'. The latter is transitory and undergoes subsequent conversion into $^{32}POCl_3$.

Chemical effects of $^{31}P(n,\gamma)^{32}P$ *reactions.* High yields of $^{32}PCl_3$ were found for the short-time irradiations, especially in samples *Q* and *R* which contained a small amount of PCl_3 added to eliminate the loss of $^{32}PCl_3$ by radiation effects.[6] In samples *Q* and *R*, 85–90 per cent of the ^{32}P was found to be in a chemical form other than $^{32}POCl_3$ indicating that chemical changes accompany most of the $^{31}P(n,\gamma)^{32}P$ reactions in liquid $POCl_3$. Even though the phosphorus atom is multiply-bonded in this compound, bond rupture due to n,γ reactions is evidently quite efficient.

The existing information on the physical processes of $^{31}P(n,\gamma)^{32}P$ reactions indicates that, primarily, chemical effects result from recoil momenta of the ^{32}P atoms. GROSHEV *et al.*[7] have reported a γ-transition diagram for ^{32}P from $^{31}P(n,\gamma)^{32}P$ reactions with thermal neutrons. Accordingly, the recoil energy accompanying emission of the initial γ-ray from ^{32}P should be in the range of 44–1050 eV, with principal energies of 770, 360, 250 and 200 eV. Furthermore, no transitions were reported which would be expected to exhibit appreciable internal conversion, a process which usually initiates multiple ionization of the parent atom.[8]

With the recoil energy of ^{32}P generally large compared to bond energies in $POCl_3$, it is of interest to ascertain the extent of bond breaking in the parent $POCl_3$ molecule.

[6] The concentration of PCl_3 in either *Q* (3·7 per cent PCl_3) or *R* (1·4 per cent PCl_3) was sufficient to protect the $^{32}PCl_3$ molecules from radiation effects but was not large enough to contribute an appreciable amount of ^{32}P activity. G values for the radiation induced exchange of phosphorus between PCl_3 and $POCl_3$ have been measured more recently in this laboratory and are about 2·4 and 1·5 for samples having compositions of *Q* and *R*. The γ-ray absorption in these samples from external γ-rays (absorption from internally-generated γ-rays may have been of comparable magnitude) was approximately $1{\cdot}4 \times 10^{18}$ eV min^{-1} g^{-1}. Thus the radiation induced exchange in *Q* amounted to about $3{\cdot}4 \times 10^{16}$ atoms g^{-1}, and the concentration of PCl_3 molecules was $4{\cdot}8 \times 10^3$ times this amount.

[7] L. B. GROSHEV, V. N. LUTSENKO, A. M. DEMIDOV and V. I. PELEKHOV, *Atlas of γ-ray Spectra from Radiative Capture of Thermal Neutrons* p. 43. Pergamon Press, London.

[8] A. H. SNELL and F. PLEASANTON, *J. Phys. Chem.* **62**, 1377 (1958).

The yields of $^{32}PCl_3$ and $^{32}POCl_3$ in samples *Q* and *R* reflect the probability of formation of these species following $^{31}P(n,\gamma)^{32}P$ reactions. Assuming that atoms connected to the phosphorus atom are lost in a random fashion, a minimum average of 3 atoms must be split away in order to yield the large fraction (approx. 4/5 for samples *Q* and *R*) of oxygen-deficient $^{32}PCl_3$ molecules which was observed.

Acknowledgements—The authors wish to express appreciation to D. W. SETSER and L. F. GRANTHAM for their assistance in this study. T. J. CLARK is grateful for a one year fellowship sponsored by the Stanolind (now Pan American) Company.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 215 to 221. Pergamon Press Ltd. Printed in Northern Ireland.

ELECTRONEGATIVITY VALUES FROM THERMOCHEMICAL DATA

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(*Received* 18 *August* 1960; *in revised form* 26 *September* 1960)

Abstract—The electronegativities of sixty-nine elements have been calculated from the most recent thermochemical data. The mean deviation of the calculated electronegativity difference, $0{\cdot}208\sqrt{\Delta}$, from the difference of the average electronegativities is 0·046 units. The trends of electronegativity values within the periodic system are summarized. The transition metal contraction, the lanthanide contraction, and crystal field stabilization are observed to contribute to the relative values of electronegativity.

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PAULING's empirical electronegativity scale[1,2] based on bond energies has been used to correlate a vast number of chemical and physical properties and has been justified theoretically to some extent.[3,4,5] PAULING[2] in 1939 proposed electronegativity values for thirty-three elements, HAISSINSKY[6] in 1946 extended the calculations to seventy-three elements (some by extrapolation), and HUGGINS[7] in 1953 re-evaluated the electronegativities of seventeen elements. The accumulation of considerable new enthalpy data for elements and compounds not previously included in calculations and the revision of some previously accepted bond energies, including E(C—C) and E(N—N), led to the present recalculation and extension of the electronegativity scale based on thermochemical data. While this work was in progress a revision of PAULING's values appeared.[8] In the present recalculation, unlike that of reference 8, the effects of the transition metal contraction and lanthanide contraction are observed; an examination is made of the consistency of the results of Pauling's two methods for evaluating "extra ionic resonance energies"; and accuracy greater than $\pm 0{\cdot}1$ electronegativity unit is demonstrated.

DATA AND CALCULATIONS

PAULING pointed out that the energy, E(A—B), of bonds between unlike atoms is usually greater than the average of the energies, E(A—A) and E(B—B), of the homoatomic bonds and that the "extra ionic resonance energy," Δ, of the heteratomic bond is related to the difference between the electron-attracting abilities of A and B.

$$\Delta = E(\text{A—B}) - \frac{E(\text{A—A}) + E(\text{B—B})}{2} \tag{1}$$

$$|\chi_A - \chi_B| = 0{\cdot}208\sqrt{\Delta} \tag{2}$$

[1] L. PAULING, *J. Amer. Chem. Soc.* **54**, 3570 (1932).
[2] L. PAULING, *Nature of the Chemical Bond*, Chap. 2. Cornell Univ. Press, Ithaca (1939).
[3] R. S. MULLIKEN, *J. Chem. Phys.* **3**, 573 (1935).
[4] R. G. PEARSON, *J. Chem. Phys.* **17**, 969 (1949).
[5] E. WARHURST, *Proc. Roy. Soc.* (London), A **207**, 32 (1951).
[6] M. HAISSINSKY, *J. Phys. Rad.um* **7**, 7 (1946).
[7] M. L. HUGGINS, *J. Amer. Chem. Soc.* **75**, 4123 (1953).
[8] L. PAULING, *Nature of the Chemical Bond* (3rd Ed.), Chap. 3. Cornell Univ. Press, Ithaca (1960).

Furthermore, it was pointed out that, for many metals, E(M—M) is unknown and that Δ can be calculated approximately from the heat of formation of MX_n by

$$\Delta = \frac{-\Delta H_f}{n} \tag{3}$$

The postulate of the arithmetic mean is employed below, since in many cases the postulate of the geometric mean is difficult to apply.[9]

In the application of the pair of equations, (1) and (2), sixteen homoatomic and thirty-eight heteratomic bond energies from the recent compilation by COTRELL[10] were employed. The average bond energies, not the bond dissociation energies, were used. Calculations involving equations (1) and (2) were made for the elements in Groups IVB to VIIB for which homoatomic, single bond energies are available. All bond energies, except E(O—O) and E(N—N), were obtained from enthalpy data for elements and binary compounds having only one type of bond to avoid making the assumption that the energy of the bond between a particular pair of elements has the same value in different compounds. Thus a few estimates of bond energies, including E(C—S), were not used. The energies of the P—P, As—As, and Sb—Sb bonds are assumed to be one-sixth of the dissociation energy, corrected for strain,[11] of the respective M_4 molecules. E(C—C) and E(Sn—Sn) are taken as one-half of the heats of atomization[12] of diamond and grey tin. The energy of the heteratomic bond, E(I—Br) tabulated in reference[10], gave an anomalous result and was not employed. The bond energies of Sb—Br, Sb—I, Cl—F, and I—Cl, not reported in reference[10] and of I—Br are taken from HUGGINS[7].

The calculations involving the pair of equations, (2) and (3), were made with values of the enthalpy of formation of halides, AX_n, in their standard states at 298°A from the elements in their standard states. One hundred and fourteen values were taken from Circular 500 of the National Bureau of Standards.[12] Two values, ΔH_{form} of CF_4 and ΔH_{form} of $AsCl_3$, were taken from COTRELL[10] instead of the older and probably inaccurate values in the NBS compilation. Also, ΔH_{form} of $GeBr_4$,[13] ΔH_{form} of GeI_4,[13] ΔH_{form} of $PbCl_4$,[14] ΔH_{form} of SCl_2,[13] were not given in the NBS compilation and were taken from other sources.

For small electronegativity differences of the bonded atoms, the ionic character increases steadily with increasing electronegativity difference. However, if $(\chi_A - \chi_B)$ is large, a further increase in the magnitude of $(\chi_A - \chi_B)$ will not greatly change the ionic character or the "extra ionic resonance energy."[4,16,17] As also done by FINEMAN and DAIGNAULT,[17] calculations of Δ leading to $(\chi_A - \chi_B) > 1{\cdot}8$ were rejected before the construction of the present thermochemical scale of electronegativity. For all potassium, rubidium and cesium halides, thermochemical data predict

[9] p. 83 of ref. 8.
[10] T. L. COTTRELL, *The Strengths of Chemical Bonds* (2nd Ed.), Chap. 8, 10, and 11, Butterworths Scientific Publications, London (1958).
[11] (a) L. PAULING, *Nature of Chemical Bond* (3rd Ed.), Chap. 3. Cornell Univ. Press, Ithaca (1960); Ref. 8. (b). W. Moffitt, *Trans. Faraday Soc.* **44**, 987 (1948). (c). Ref. 7.
[12] F. D. ROSSINI *et al. Selected Values of Chemical Thermodynamic Properties* (Circular 500 of the National Bureau of Standards), U.S. Government Printing Office, Washington, D.C. (1952).
[13] D. E. EVANS and R. E. RICHARDS, *J. Chem. Soc.* 1292 (1952).
[14] F. YAKULHA, *J. Gen. Chem.* U.S.S.R. (English Translation) **24**, 1677 (1954).
[15] L. BREWER, L. A. BROMLEY, P. W. GILLES and N. L. LOFGREN, National Nuclear Energy Series, Div. IV, *19B*, 76 (1960).
[16] L. PAULING, *Nature of the Chemical Bond*, p. 61. Cornell Univ. Press, Ithaca (1939).
[17] M. A. FINEMANN and R. DAIGNAULT, *J. Inorg. Nucl. Chem.* **10**, 205 (1959).

that ($\chi_X - \chi_M$) is greater than 1·8 and values for these three metals were estimated from ΔH_{form} of the iodides in which ($\chi_X - \chi_M$) ranges from 1·84 to 1·87. In some cases, Δ appeared to be a minus quantity and ($\chi_A - \chi_B$) could not be estimated. For example, Δ for hydrogen sulphide is −16·6 kcal/mole. The value of 2·53 for the electronegativity of silver in silver fluoride may be anomalous and is not included in Table 2 or in the calculation of the average electronegativity of silver.

In Tables 1 and 2, the electronegativity values for the elements at the left were obtained by assuming the average electronegativity value of the chemically bonded element at the top. Equation (1) gives the values in parentheses, and equation (3) gives the other values. Electronegativity values (not presented here explicitly) for the halogens in compounds with the metals listed in Table 2 were calculated from Δ and $\chi_{M(Av.)}$ and used in the determination of the average electronegativities of the halogens. The value of 2·20 for hydrogen was given by HUGGINS[7] and was assigned here as the basis of the scale of relative electronegativities. The average electronegativity values are presented in Table 3. The oxidation numbers exhibited by elements in compounds included in these calculations are given in the first row of Table 3. Thus the electronegativity values in this table are for specified oxidation states. Electronegativity values of some elements in other oxidation states were calculated, assuming the average electronegativities of the halogens in Table 3, and are presented in Table 4.

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DISCUSSION AND RESULTS

A total of 162 computations were made in the evaluation of electronegativities for sixty-nine elements. Electronegativity values for twenty-six elements were assigned on the basis of only one computation; and for the remaining forty-three elements and one hundred and thirty-six computations, the mean deviation of the calculated electronegativity difference, $0{\cdot}208\sqrt{\Delta}$, from the difference of the average electronegativities ($\chi_A - \chi_B$) is 0·046 units. In a tabulation of calculated electronegativities published in 1953,[7] the mean deviation was 0·062 units for seventeen elements and fifty-four computations. In view of the concept of orbital electronegativity,[18] uncertainties in the enthalpy and bond energy data, and the complexity of factors contributing to heats of formation, a mean deviation of 0·046 units is remarkably small. Certainly, each element exhibits a range of electronegativities greater than 0·01.[18]

The validity of substituting the approximate equation (3), for equation (1) has been discussed elsewhere.[2,6,17,18] PAULING pointed out[19] that equation (3) is applicable if the van der Waals stabilization and other factors contributing to the enthalpy have the same magnitude for the elements as for the product. For eighteen bonds, Δ was computed by equation (1) and by equation (3), and the results are presented in Table 5. The average values of Δ for these eighteen bonds are 21·5 kcal and 22·0 kcal for equations (1) and (3), respectively. The average difference between the two Δ values for each bond is 1·9 kcal. Thus the results from equations (1) and (3) are mutually consistent.

Electronegativity values decrease monotonically within the groups, Li–Na–K–Rb–Cs, Be–Mg–Ca–Sr–Ba, Sc–Y–La, N–P–As–Sb–Bi,* O–S–Se, F–Cl–Br–I. Alternation in electronegativity values is observed in the groups, B–Al–Ga–In–Tl and

* There is considerable evidence (ALLRED and HENSLEY[20]) that the electronegativity of bismuth is considerably higher than the value reported here on the basis of ΔH_{form} of bismuth trichloride.

[18] H. O. PRITCHARD and H. A. SKINNER, *Chem. Rev.* **55**, 745 (1955).
[19] L. PAULING, *Nature of the Chemical Bond*, p. 63. Cornell Univ. Press, Ithaca (1939).
[20] A. L. ALLRED and A. L. HENSLEY, *J. Inorg. Nucl. Chem.* **17**, 43 (1961).

TABLE 1.—CALCULATED ELECTRONEGATIVITIES

	H	C	Si	Ge	Sn	Pb	N	P	As	Sb	Bi	O	S	Se	F	Cl	Br	I
H		(2·11)					(2·07)					(2·11)	(2·17)		(2·31)	(2·18)	(2·22)	(2·42)
C	(2·64)		(2·44)												2·44 (2·44)	2·56 (2·63)	(2·65)	
Si		(2·01)										(1·78)	(1·74)			1·87 (1·92)	1·93 (1·93)	2·08 (1·96)
Ge																1·97 (2·02)	2·02 (2·02)	2·08 (1·98)
Sn																1·96 (2·04)	1·92 (1·93)	
Pb															2·43	2·24		
N	(3·17)														(2·90)			
P												(2·19)			(2·22)	2·08 (2·19)	2·12 (2·20)	2·26
As												(2·22)			(2·21)	2·14 (2·19)	2·13 (2·13)	2·21 (2·16)
Sb												(2·16)				2·01 (2·04)	2·00 (1·95)	2·08 (1·99)
Bi																2·02		
O	(3·55)		(3·56)					(3·44)	(3·40)	(3·33)					(3·34)	(3·50)		
S	(2·61)		(2·74)													2·38		
Se																(2·55)		
F	(3·87)	4·09 (4·09)				3·88	(4·12)	(3·95)	(3·95)			(4·08)				(3·92)		
Cl	(3·18)	3·15 (3·08)	3·19 (3·14)	3·20 (3·15)	3·16 (3·08)	3·25		3·27 (3·16)	3·20 (3·15)	3·20 (3·17)	3·16	(3·10)	3·36	(3·16)	(3·22)			(3·04)
Br	(2·93)	(2·86)	2·92 (2·93)	2·95 (2·95)	2·99 (2·98)			3·02 (2·94)	3·00 (3·00)	3·00 (3·05)								(2·91)
	(2·44)		2·48 (2·60)	2·59 (2·69)				2·59	2·63 (2·68)	2·63 (2·72)						(2·78)	(2·70)	

TABLE 2.—CALCULATED ELECTRONEGATIVITIES

	Cl	Br	I		Cl	Br	I
Li			0·98	Ti	1·59	1·52	1·51
Na			0·93	Zr	1·39	1·34	1·26
K			0·82	V	1·63		
Rb			0·82	Cr	1·73		1·59
Cs			0·79	Mo	2·18	2·16	2·15
Be	1·53	1·57	1·61	W	2·25	2·31	2·51
Mg		1·32	1·30	Mn	1·58	1·55	1·53
Ca			1·00	Fe	1·83	1·81	1·85
Sr			0·95	Co	1·86	1·85	1·93
Ba			0·89	Ni	1·88	1·87	1·99
Sc	1·37	1·34		Rh	2·28		
Y			1·22	Pd	2·17	2·22	
La			1·10	Ir	2·20		
Ce			1·12	Pt	2·28		
Pr			1·13	Cu	1·98	1·91	1·82
Nd			1·14	Ag	2·01	1·93	1·86
Sm			1·17	Au	2·56	2·51	
Gd			1·20	Zn	1·69	1·65	1·62
Dy			1·22	Cd	1·74	1·68	1·64
Ho			1·23	Hg	2·07	2·01	1·92
Er			1·24	B	1·99	2·08	
Tm			1·25	Al	1·61	1·60	1·62
Lu			1·27	Ga	1·82	1·80	1·80
U	1·40	1·38	1·37	In	1·80	1·77	1·77
Np	1·39	1·36	1·34	Tl	2·06	2·03	
Pu		1·30	1·27				

TABLE 3.—AVERAGE ELECTRONEGATIVES*

I	II	III	II	II	II	II	II	II	II	I	II	III	IV	III	II	I
H 2·20																
Li 0·98	Be 1·57											B 2·04	C 2·55	N 3·04	O 3·44	F 3·98
Na 0·93	Mg 1·31											Al 1·61	Si 1·90	P 2·19	S 2·58	Cl 3·16
K 0·82	Ca 1·00	Sc 1·36	Ti 1·54	V 1·63	Cr 1·66	Mn 1·55	Fe 1·83	Co 1·88	Ni 1·91	Cu 1·90	Zn 1·65	Ga 1·81	Ge 2·01	As 2·18	Se 2·55	Br 2·96
Rb 0·82	Sr 0·95	Y 1·22	Zr 1·33		Mo 2·16			Rh 2·28	Pd 2·20	Ag 1·93	Cd 1·69	In 1·78	Sn 1·96	Sb 2·05	Te	I 2·66
Cs 0·79	Ba 0·89	La 1·10	Hf		W 2·36			Ir 2·20	Pt 2·28	Au 2·54	Hg 2·00	Tl 2·04	Pb 2·33	Bi 2·02		
		Ce 1·12	Pr 1·13	Nd 1·14	Pm	Sm 1·17	Eu	Gd 1·20	Tb	Dy 1·22	Ho 1·23	Er 1·24	Tm 1·25	Yb	Lu 1·27	
					U 1·38	Np 1·36	Pu 1·28									

* The oxidation state is specified at the top of each group.

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TABLE 4.—ELECTRONEGATIVITIES OF SOME ELEMENTS IN DIFFERENT OXIDATION STATES

Mo^{II}	2·18	Mo^{V}	2·27	Tl^{I}	1·62
Mo^{III}	2·19	Mo^{VI}	2·35	Sn^{II}	1·80
Mo^{IV}	2·24	Fe^{III}	1·96	Pb^{II}	1·87

TABLE 5.—VALUES OF Δ CALCULATED BY TWO METHODS

	(Eq. 1) (kcal)	(Eq. 3) (kcal)		(Eq. 1) (kcal)	(Eq. 3) (kcal)
CF_4	54·7	54·5	$SnBr_4$	24·0	24·3
CCl_4	6·5	8·3	PCl_3	21·8	27·0
$SiCl_4$	35·5	38·2	PBr_3	12·8	15·8
$SiBr_4$	24·5	23·8	$AsCl_3$	21·8	23·8
SiI_4	11·5	7·9	$AsBr_3$	15·7	15·5
$GeCl_4$	29·6	32·5	AsI_3	5·7	4·6
$GeBr_4$	20·5	20·4	$SbCl_3$	29·0	30·4
GeI_4	10·5	7·6	$SbBr_3$	23·0	20·7
$SnCl_4$	29·1	32·6	SbI_3	10·0	7·7
			Average:	21·5	22·0

C–Si–Ge–Sn–Pb. Chemical and physical evidence for the alternation in Group IVB has been presented previously.[21,22,23] The alternation is explainable in terms of the transition metal contraction and the lanthanide contraction. These contractions lead to a greater force of attraction between the nucleus and the electrons at the covalent boundary of the atom.[22] In building up the fourth row of the periodic system, increasing nuclear charge accompanies the filling of the inner 3*d* subshell and causes gallium and germanium to be more compact (although not smaller) than aluminium and silicon. Similarly, in building up the sixth row, increasing nuclear charge is balanced by electrons entering the 4*f* subshell. Thus the elements to the right of hafnium are more compact and more electronegative than the elements in corresponding groups in the fifth row. The effects of the transition metal and lanthanide contractions steadily become less pronounced with increasing group number, IIIB IVB VB VIB VIIB, due to additional electrons in the ultimate *s* and *p* subshells. In fact, the nitrogen group (VB) marks the transition from alternation to monotonic change of electronegativity.

The electronegativities of the lanthanides increase slightly and steadily with increasing atomic number. This trend with increasing atomic number parallels, as expected, the decrease in basicity of the trihydroxides, the increase in the ease of complex formation, and the decrease of the standard electrode potentials. In the actinide series, the electronegativity increases from plutonium to neptunium to uranium with a corresponding decrease in the standard electrode potentials, Pu: 2·03V, Np: 1·83V and U: 1·80V.[24]

The variation of the electronegativities of the elements from calcium to zinc reflects the increase in nuclear charge and the magnitude of the crystal field stabilization

[21] R. T. SANDERSON, *J. Amer. Chem. Soc.* **74**, 4792 (1952).
[22] A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 264 (1958).
[23] A. L. ALLRED and E. G. ROCHOW, *J. Inorg. Nucl. Chem.* **5**, 269 (1958).
[24] J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements*, p. 412, J. Wiley, New York (1957).

energy. In the metal ions in which crystal field stabilization is important, the electronic charge is concentrated in orbitals directed away from ligands; and, therefore, the nuclear charge of the metal is especially effective in attracting electrons from bonded ligands. Thus in the series from calcium to zinc, the relatively low electronegativity values for divalent calcium, manganese, and zinc are explained by the spherically symmetric distribution of charge on the metal ions. The variation of electronegativity in this series is comparable to the variation in the heat of hydration[25] of the divalent ions, the lattice energies of the dihalides,[26] and the sum of the first and second ionization potentials.[26]

Recently, an attempt[17] to evaluate electronegativities with a modification of PAULING's equation led to results which differ considerably from those reported here for several metals. The modified equation utilizes data pertaining to two metal halides and does not require the energy of the metal–metal bond. However, the modified equation contains a term having $(\chi_X - \chi_{X'})$ in the denominator, and a small error in the electronegativity of either of the halogens, X or X′, leads to a considerable uncertainty in the calculated electronegativity of the metal. Since each element actually has a small range of electronegativity values instead of an invariant value,[18] small uncertainties in the electronegativities of the halogens are expected.

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Since PAULING's recent electronegativities are reported to two significant figures, compared with three in the present recalculation, an apparently close agreement of the values in the two scales is expected. However, the value for lead, 2·33, differs considerably from the value of 1·8 reported by PAULING in reference 8. There is considerable evidence for the high electronegativity of lead.[3] PAULING's values for zinc, gallium, germanium, and arsenic are surprisingly low and do not reflect the transition metal contraction. For a few other values, there are small discrepancies the origin of which is obscure since in reference 8 there is an incomplete tabulation of the compounds and enthalpy data applied in the calculations.

The scale of electronegativies from thermochemical data in Table 3 can be compared readily with scales of electronegativities obtained from other properties. Several scales of electronegativities are listed in reviews by PRITCHARD and SKINNER[18] and by GORDY and THOMAS,[27] and a scale of electronegativity based on electrostatic force is presented in reference 22. There is a remarkably close agreement of the values obtained from quite different properties for many elements, and practically all of the disagreements can be traced to the approximate nature of the relations between electronegativities and the properties being observed.

[25] L. BREWER, L. A. BROMELY, P. W. GILLES and N. L. LOFGREN, *Chemistry and Metallurgy of Miscellaneous Materials*, p. 165 ff.(Edited by L. L. QUILL) McGraw-Hill, New York (1950).
[26] F. BASOLO and R. G. PEARSON, *Mechanisms of Inorganic Reactions*, pp. 66 and 71. Wiley, New York (1958).
[27] W. GORDY and W. J. O. THOMAS, *J. Chem. Phys.* **24**, 439 (1956).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 222 to 231. Pergamon Press Ltd. Printed in Northern Ireland

THE ABSORPTION SPECTRA OF COMPLEX SALTS—IV

CUPRIC ALKANOATES

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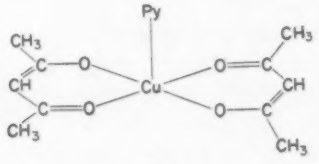
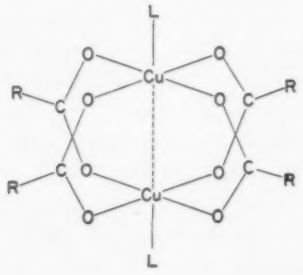
(*Received* 6 *July* 1960)

Abstract—The low-intensity absorption spectra of dimeric cupric alkanoates in chloroform solution may be resolved into Gaussian components with frequencies of about 1·1, 1·4 and 2·7 μ^{-1}, similar to those of the pyridine adducts of cupric β-diketone complexes. The frequencies of these bands are independent of variation in the alkanoate anions, but shift to higher frequencies with axial ligands of increasing donor power, consistent with their interpretation as triplet–triplet ligand-field bands, the superimposed singlet-triplet transition energy being too small to be observed experimentally. High-intensity absorption at a frequency of about 4μ^{-1}, sensitive to changes of the alkanoate ion but not to changes in the axial ligands, is attributed to charge-transfer processes.

IN Part III[1] the absorption spectra of planar cupric complexes, such as the acetylacetonate or ethyl-acetoacetate, were resolved into three ligand-field bands with frequencies of about 1·4, 1·8 and 2·7μ^{-1}, in addition to high-intensity absorption at higher frequencies. The shift of the ligand-field bands to frequencies of about 1·1, 1·4 and 2·7 μ^{-1} on addition of pyridine was regarded as consistent with the formulation of the 1:1 pyridine adducts as 5:co-ordinated tetragonal pyramidal structures (I).[2]



I



II

Fully-resolved absorption spectra are now reported for a range of dimeric cupric alkanoates in non-donor solvents with alkanoic acids, pyridine, dioxane or water as axial ligands (L in structure II), the electro-static environment of the copper atoms being tetragonal-pyramidal throughout. In all cases absorption in the 1–3μ^{-1} region can be resolved into three Gaussian components with frequencies of about 1·1, 1·5 and 2·7μ^{-1}, thus supporting the stereochemistry suggested for the pyridine adducts (I). Additional high-intensity absorption at a frequency of 3·9–4·0μ^{-1} is attributed to

[1] D. P. GRADDON, *J. Inorg. Nucl. Chem.* **14**, 161 (1960).
[2] D. P. GRADDON, *Nature, Lond.* **183**, 1610 (1959).

charge-transfer processes, since alkanoate ions show only weak absorption below about $5\mu^{-1}$.

All of the results reported below are for solutions in chloroform, but no significant difference was observed in numerous comparison experiments using benzene or cyclohexane as solvents, so that solvent participation in the absorbing species can be discounted.

ANALYSIS OF ABSORPTION SPECTRA

(1) *Solutions containing free alkanoic acids*

Anhydrous cupric alkanoates are insoluble in chloroform and other non-donor solvents, although some of the higher homologues may become dispersed;[3] they

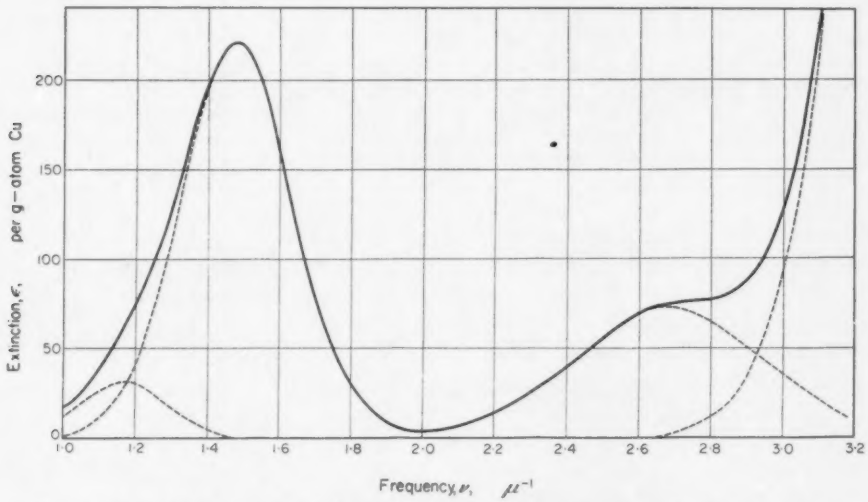


FIG. 1.—Gaussian components of absorption spectrum of cupric n-octoate (10^{-3} g-atom. Cu/l.) in chloroform containing n-octoic acid (5×10^{-2} mole/l.)

dissolve readily, however, in the presence of free alkanoic acids. Persistence of the dimeric structure in these solutions is shown by partition experiments with cupric propionate[4] and by solubility measurements with the acetate, isobutyrate and crotonate in the presence of varying concentrations of the corresponding acids. Such equilibrium experiments also show that the dissolved species are the alkanoic acid solvates (II, L = R.COOH).[5]

The absorption spectra of these solutions are remarkably independent of changes in the alkanoic acids; even substitution by halogen, aryl or unsaturated groupings produces changes which are barely significant. In each case a strong absorption band ($\varepsilon \sim 200$) at a frequency of about $1{\cdot}47\mu^{-1}$ (wavelength about 680 mμ) resolves into two Gaussian components at about $1{\cdot}47\mu^{-1}$ ($\varepsilon \sim 200$) and $1{\cdot}15\mu^{-1}$ ($\varepsilon \sim 30$), and a shoulder on the ultra-violet high-intensity band can be resolved into a third Gaussian curve at about $2{\cdot}68\mu^{-1}$ ($\varepsilon \sim 60$). The resolution of a typical absorption spectrum is

[3] R. L. MARTIN and A. WHITLEY, *J. Chem. Soc.* 1394 (1958).
[4] D. P. GRADDON, *J. Inorg. Nucl. Chem.* **11**, 337 (1959).
[5] D. P. GRADDON, *Nature, Lond.* **186**, 715 (1960).

shown in Fig. 1 and Table 1 gives the parameters of the Gaussian components of the absorption spectra for twelve different alkanoic acids.

(2) *Solutions containing free alkanoic acids and pyridine*

Addition of pyridine to cupric alkanoate/alkanoic acid solutions displaces the main absorption peak at 680 mμ to longer wavelengths, while retaining the absorption

TABLE 1.—LIGAND-FIELD BANDS OF CUPRIC ALKANOATE/ALKANOIC ACID ADDUCTS IN CHLOROFORM

Acid	ν_1 (μ^{-1})	ε	Width (μ^{-1})	ν_2 (μ^{-1})	ε	Width (μ^{-1})	ν_3 (μ^{-1})	ε	Width (μ^{-1})
Acetic	1·16	21	0·30	1·475	182	0·34	2·67	45	0·52
Propionic	1·14	26	0·28	1·475	212	0·36	2·68	66	0·62
n-Butyric	1·14	25	0·31	1·475	212	0·36	2·67	57	0·58
n-Valeric	1·17	30	0·30	1·475	224	0·35	2·66	60	0·54
n-Caproic	1·15	32	0·30	1·48	230	0·36	2·68	66	0·64
n-Octoic	1·16	36	0·28	1·48	220	0·36	2·68	72	0·62
Isobutyric	1·14	25	0·30	1·475	224	0·37	2·65	87	0·66
Pivalic	1·13	24	0·26	1·485	232	0·38	2·65	78	0·60
β-Chloro-propionic	1·15	26	0·28	1·46	222	0·38	2·72	50	0·66
β-Phenyl-propionic	1·14	28	0·24	1·48	200	0·37	2·68	68*	0·66
Phenylacetic	1·14	32	0·28	1·46	234	0·36	2·66	88*	0·64
Crotonic	1·15	32	0·28	1·475	228	0·35	2·68	52*	0·60

* Experimental curve shows only an inflexion.

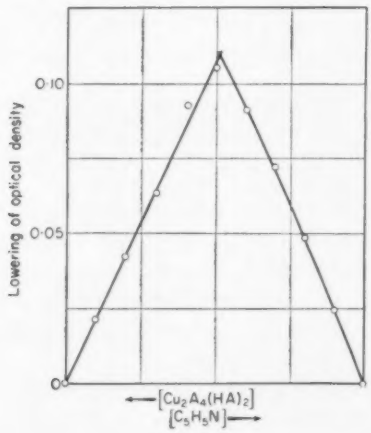


FIG. 2.

pattern characteristic of the dimeric structure (II). The stoicheiometry of the dissolved species is shown by continuous variation studies (Fig. 2) and, since the absorption of solutions of the cupric alkanoate hydrates in chloroform containing pyridine are the same as those obtained in the presence of alkanoic acids, it is apparent that the pyridine molecules displace the molecules of alkanoic acids occupying axial positions to give the pyridine solvates (II, L = pyridine). The acetate solvate, $Cu_2(OCOCH_3)_4(C_5H_5N)_2$,

has been obtained in the solid state and shown by X-ray analysis[6] to have the cupric acetate type of structure.

The absorption of the pyridine solvates is very similar to that of the alkanoic acid solvates, except for a slight shift of all of the Gaussian component bands to lower frequencies (about 1·04, 1·41 and 2·64μ^{-1}), a slight reduction of the intensities of the two bands of lower frequency and a slightly increased intensity in the band of highest

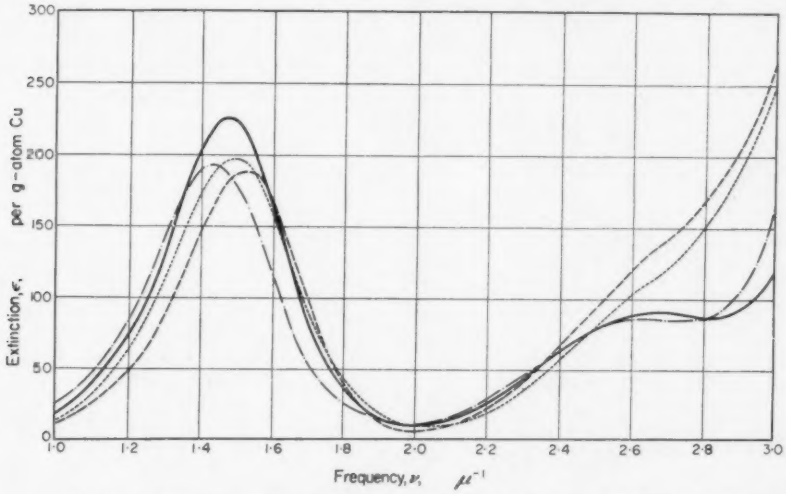


FIG. 3.—Absorption spectra of cupric isobutyrate in chloroform solutions containing
isobutyric acid ————
pyridine — — — — —
dioxane – – – – –
and of a chloroform solution of cupric isobutyrate hydrate. . . . .

TABLE 2.—LIGAND-FIELD BANDS OF CUPRIC ALKANOATE/PYRIDINE ADDUCTS IN CHLOROFORM

Acid	ν_1 (μ^{-1})	ε	Width (μ^{-1})	ν_2 (μ^{-1})	ε	Width (μ^{-1})	ν_3 (μ^{-1})	ε	Width (μ^{-1})
Acetic	1·07	19	0·34	1·41	160	0·34	2·65	49	0·52
Propionic	1·04	23	0·30	1·415	192	0·36	2·65	69	0·56
n-Butyric	1·04	20	0·30	1·415	190	0·38	2·63	69	0·56
n-Valeric	1·03	18	0·30	1·415	198	0·38	2·63	75	0·56
n-Octoic	1·04	27	0·22	1·41	226	0·38	2·65	87	0·58
Isobutyric	1·05	20	0·32	1·43	192	0·39	2·62	82	0·7
Pivalic	1·04	24	0·3	1·41	180	0·36	2·64	80*	0·56

* Experimental curve shows only an inflexion.

frequency (Fig. 3). The parameters of the component bands are given in Table 2 for seven alkanoic acids.

(3) *Solutions containing dioxane*

Persistence of the dimeric cupric alkanoate structure in dioxane solutions was shown by MARTIN and WATERMAN's cryoscopic measurements.[3] A continuous

[6] G. A. BARCLAY and C. H. L. KENNARD. Private communication.

variation study (Fig. 4) shows that the actual species in solution are the solvated dimers, $Cu_2(OCOR)_4(C_4H_8O_2)_2$, as confirmed by the observation that the same absorption spectra are obtained from solutions of anhydrous or hydrated cupric alkanoates in dioxane or in chloroform on the addition of dioxane.

These absorption spectra resolve into three Gaussian components with frequencies slightly higher than those of the alkanoic acid adducts (about 1·19, 1·51 and 2·7μ^{-1});

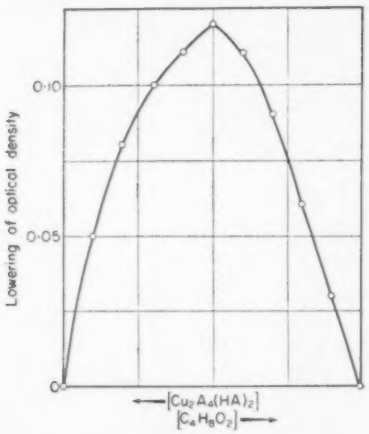


FIG. 4.

TABLE 3.—LIGAND-FIELD BANDS OF CUPRIC ALKANOATE/DIOXANE ADDUCTS IN CHLOROFORM

Acid	ν_1 (μ^{-1})	ε	Width (μ^{-1})	ν_2 (μ^{-1})	ε	Width (μ^{-1})	ν_3 (μ^{-1})	ε	Width (μ^{-1})
Acetic	1·15	15	0·26	1·51	115	0·38	2·7	60*	0·7
Propionic	1·18	25	0·26	1·51	178	0·36	2·72	70*	0·62
n-Octoic	1·20	29	0·27	1·52	211	0·35	2·72	80*	0·66
Isobutyric	1·18	22	0·28	1·52	150	0·36	2·75	106*	0·68
β-Chloro-propionic	1·14	30	0·28	1·49	159	0·36	2·8	120*	0·8

* Experimental curve shows only an inflexion.

extinctions are lower in the two bands of lower frequency, but those of the band at 2·7μ^{-1} are probably higher, though the resolution of this band is less satisfactory than in the two previous cases, as it is more deeply embedded in the high-intensity ultraviolet absorption band (Fig. 3). Parameters of the Gaussian component bands for five alkanoic acids are given in Table 3.

(4) *Solutions of hydrated cupric alkanoates*

Whereas cupric acetate hydrate (II, R = CH_3, L = H_2O) is quite insoluble in organic solvents such as chloroform, benzene or cyclohexane, the hydrates of its higher homologues dissolve to a greater or lesser extent, and those of the homologues higher than butyric acid are freely soluble without separation of water or precipitation due to hydrolysis; in some instances, e.g. the isobutyrate, pivalate or octoate, the

hydrates can be recrystallized from dry benzene. Since the anhydrous compounds are insoluble, these solutions must clearly contain the hydrated dimeric molecules as solute species.

TABLE 4.—LIGAND-FIELD BANDS OF CUPRIC ALKANOATE HYDRATES IN CHLOROFORM SOLUTION

Acid	ν_1 (μ^{-1})	ε	Width (μ^{-1})	ν_2 (μ^{-1})	ε	Width (μ^{-1})	ν_3 (μ^{-1})	ε	Width (μ^{-1})
Propionic	1·12	17	0·22	1·48	170	0·38	2·61	41	0·56
n-Octoic	1·11	16	0·22	1·48	172	0·44	2·8	66*	0·7
Isobutyric	1·14	14	0·26	1·49	156	0·40	2·8	100*	0·7
Pivalic	1·1	7	0·22	1·50	126	0·44	2·8	100*	0·7
β-Chloro-propionic	1·14	24	0·28	1·46	183	0·36	2·64	41	0·56

* Experimental curve shows only an inflexion.

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The absorption spectra of these solutions resemble closely those of solutions containing alkanoic acids, pyridine or dioxane, and can be resolved into three Gaussian component bands with frequencies nearly identical with those of the alkanoic acid solvates (about 1·13, 1·48 and 2·7 μ^{-1}), although the extinctions are lower (Fig. 3). The parameters of these component bands are shown in Table 4 for five different acids.

(5) *High intensity absorption in the region of* $4\mu^{-1}$ (250 mμ)

The frequency and extinctions of these bands are shown in Table 5 for seven different cupric alkanoates in the presence of a variety of axial solvating ligands. All the results are in chloroform solution, but there appears to be no significant solvent effect. Owing to the cutting off of the absorption band by the heavy absorption of the solvent on the high-frequency side it is not possible to test how closely these curves approximate to Gaussian.

DISCUSSION

From MARTIN and WATERMAN's magnetic studies[7] it is apparent that in the dimeric cupric alkanoate structure some electron pairing occurs by interaction of the '*d*'-electrons of neighbouring copper atoms (δ-bond formation), resulting in a partial quenching of the magnetic moment, so that the actual state can be regarded as a mixture of the singlet and triplet states. The absorption spectrum must thus be complicated by the superposition of the singlet–triplet transition on the ligand-field bands. However, the singlet–triplet transition energy is so small—about $0{\cdot}03\mu^{-1}$ (300 cm^{-1})—that its effect on the ligand-field bands will scarcely be within the experimentally detectable range. As ROSS suggests,[8] it should be possible to disentangle these effects by observations of the absorption spectra at widely different temperatures, but unfortunately the temperature range experimentally available in solution in one solvent is not sufficient to make significant differences to the proportions of molecules in the singlet and triplet states.

[7] R. L. MARTIN and H. WATERMAN, *J. Chem. Soc.* 2545 (1957).
[8] I. G. ROSS and J. YATES, *Trans. Faraday Soc.* **55**, 1057, 1064 (1959).

In the present analysis therefore, the absorption bands will be treated as triplet–triplet ligand-field bands, though each such band is presumably made up of two components differing in frequency by about $0{\cdot}03\mu^{-1}$, the proportions of such components being nearly constant throughout.

From the viewpoint of ligand-field theory, since the symmetry of the molecules ensures that neither copper atom is charged relative to the other, the electrostatic ligand-field round each copper atom is tetragonal-pyramidal, the field at the apex of

TABLE 5.—HIGH-INTENSITY ULTRA-VIOLET ABSORPTION BANDS OF CUPRIC ALKANOATES IN CHLOROFORM SOLUTION

Alkanoic acid	Axial ligand	ν_4 (μ^{-1})	$\varepsilon \times 10^{-3}$
Acetic	acetic acid	4·01	5·3
Propionic	propionic acid	3·94	6·7
	pyridine*	3·94	4·7
	dioxane	3·94	5·2
	water	3·95	3·6
n-Butyric	n-butyric acid	3·90	6·3
	pyridine*	3·88	6·5
n-Valeric	n-valeric acid	3·88	6·5
	pyridine*	3·88	6·7
n-Octoic	n-octoic acid	3·91	7·5
	water	3·92	5·8
Isobutyric	isobutyric acid	3·88	6·9
	water	3·87	5·3
Pivalic	pivalic acid	3·87	7·0
	water	3·87	5·4

* Corrected for the heavy background absorption due to the pyridine.

the pyramid being much smaller than that at the four equivalent corners and particularly sensitive to variation of the axial ligands. The environment of each copper atom is thus similar to that in a square planar complex to which one additional ligand has been added in the axis normal to the plane.

Resolution of the absorption of the axially-solvated dimeric cupric alkanoates into three bands at about 1·1, 1·4 and $2{\cdot}7\mu^{-1}$, as was found for the cupric β-diketone/pyridine adducts (I), thus provides strong support for the tetragonal-pyramidal structure proposed for these adducts. In them the above transitions were tentatively assigned to the $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, and $d_{xz,yz} \rightarrow d_{x^2-y^2}$ transitions respectively, taking into account the observations of YAMADA *et al.*[9,10] on the polarization of the absorption bands of crystalline hydrated cupric acetate and some of its homologues at 1·4 and $2{\cdot}7\mu^{-1}$.

If these assignments are correct we should expect changes in the axial solvating ligand (L in Structure II) to produce shifts which would be most pronounced in the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition, since the d_{z^2} orbital points directly at these ligands; and since the energy of the d_{z^2} orbital should be raised furthest by those axial ligands which produce the highest ligand-fields, the transition energy $d_{z^2} \rightarrow d_{x^2-y^2}$ should be lowest with such ligands. Table 6 shows the mean transition energies of the ligand-field

[9] R. TSUCHIDA and S. YAMADA, *Nature, Lond.* **176**, 1171 (1955).
[10] R. TSUCHIDA, S. YAMADA and N. NAKAMURA, *Nature, Lond.* **181**, 479 (1958).

bands, the axial ligands being arranged as nearly as possible in order of increasing ligand-field effect. It will be noted that the transition energies are almost independent of variations in the alkanoate anions (Tables 1–4).

The decrease in the transition energies as the axial ligand changes from dioxane to pyridine is apparent in all three bands, but is both relatively and absolutely greatest in the $1{\cdot}1\mu^{-1}$ band in agreement with its assignment to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The resolution of the $2{\cdot}7\mu^{-1}$ band is not good enough when dioxane or water occupy the axial sites for comparisons to be made of the effects of the axial ligands on the other two transitions.

TABLE 6.—MEAN LIGAND-FIELD TRANSITION ENERGIES WITH DIFFERENT AXIAL SOLVATING LIGANDS

Axial ligand	ν_1 (μ^{-1})	ν_2 (μ^{-1})	ν_3 (μ^{-1})
Dioxane	1·19	1·51	2·7
Water	1·13	1·48	2·7
Alkanoic acids	1·15	1·47	2·68
Pyridine	1·04	1·41	2·64

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It is significant that, unlike the ligand-field bands, the frequency of the absorption band in the $4\mu^{-1}$ region is not affected by variation in the axial solvating ligands, but is sensitive to changes in the alkanoate anions, at least in the early members of the series (Table 5). The absorption band in this region is thus attributed to charge–transfer processes of the type:

$$RCOO^- + Cu^{++} = RCOO\cdot + Cu^+$$

This assignment is supported by the improbability of high-intensity absorption by the anions at frequencies much below $5\mu^{-1}$. Observation of the absorption in cyclohexane solution shows that there is no further absorption band at frequencies below $4{\cdot}6\mu^{-1}$.

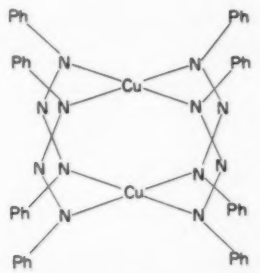
The location of charge–transfer bands at $3{\cdot}9$–$4{\cdot}0\mu^{-1}$ in the cupric alkanoates raises again the question of the assignment of the high-intensity ultra-violet absorption bands of the cupric β-diketone complexes previously atrributed to the *K*-bands of the ligand-enol anions.[1,11] It now seems more probable that this absorption should be attributed in part to the *K*-bands of the ligands and in part to charge–transfer processes. In a theoretical calculation BELFORD *et al.*[11] show that the absorption band of the acetylacetonate anion can be expected to move from $3{\cdot}7\mu^{-1}$ to lower frequencies on co-ordination, and this is confirmed by the observation that in the acetylacetonates of zinc and magnesium this band appears at about $3{\cdot}4\mu^{-1}$, with no further absorption below $4{\cdot}6\mu^{-1}$. Of the two high-intensity bands of cupric acetylacetonate which appear in chloroform solution at 3·4 and $4{\cdot}1\mu^{-1}$, the former is thus assigned to the *K*-band of the ligand and the latter to charge–transfer. In cupric ethyl-acetoacetate the corresponding bands appear at 3·8 and $4{\cdot}3\mu^{-1}$. The charge–transfer bands in all these compounds thus appear in the narrow range $3{\cdot}9$–$4{\cdot}3\mu^{-1}$, which agrees well with the close similarity of the ligands, all of which possess alternate donor oxygen atoms of ketonic and enolic type.

[11] R. L. BELFORD, A. E. MARTELL and M. CALVIN, *J. Inorg. Nucl. Chem.* **2**, 11 (1956).

Cupric alkanoates and the cupric complexes of β-diketones thus provide examples of 4: and 5:co-ordinated Cu^{++} with ligands of closely similar nature, for which the location of the ligand-field bands is highly characteristic:

4:co-ordination	about 1·4, 1·8 and 2·7μ^{-1}
5:co-ordination	about 1·1, 1·4 and 2·7μ^{-1}.

Application of these criteria should give additional information concerning the nature of cupric complexes in solution.



III

HARRIS *et al.*,[12] for example, have proposed a structure (III) analogous to the cupric acetate structure for the cupric salt of diazominobenzene, in which 5:co-ordination is sterically obstructed, so that the ligand-field environment of the copper atoms is square planar. Any absorption band which might appear at 2·7μ^{-1} is obscured by the high-intensity absorption of the ligand, but the published absorption spectrum in the visible region can be resolved into two bands at about 1·5 and 1·9μ^{-1}, supporting the square planar ligand-field and the proposed structure, and providing an example of ligand-field bands at 1·5 and 1·9μ^{-1} in a structure of the cupric acetate type.

EXPERIMENTAL

(1) *Preparation of cupric alkanoates*

All were prepared by adding one equivalent of aqueous cupric sulphate solution to one equivalent of an aqueous solution of the appropriate sodium salt containing a small quantity of free alkanoic acid to suppress hydrolysis. The precipitated cupric salts were filtered off, dried at the pump, then over sodium hydroxide *in vacuo*. By this method cupric crotonate, phenylacetate and β-phenylpropionate were obtained anhydrous and all the other salts as monohydrates.

Crystalline hydrated cupric acetate, propionate and β-chloropropionate were obtained by recrystallization from aqueous solutions of the corresponding acids, the crystals being dried over sodium hydroxide. Hydrates of the higher homologues were recrystallized from benzene containing a small amount of the corresponding alkanoic acid. Crystalline anhydrous cupric acetate was obtained by dissolving the hydrate in a mixture of acetic acid and acetic anhydride and slowly distilling away the acetic acid through a fractionating column, when the anhydrous salt was deposited as the acetic acid was removed. Crystalline anhydrous cupric propionate was obtained by recrystallization of the hydrate from propionic anhydride. Anhydrous salts of the higher homologues were obtained by desiccation of the hydrates over phosphorus pentoxide in a drying pistol heated by boiling water.

Analyses. The compositions of all of the products were checked by iodimetric determination of the copper contents. These analyses are compared with the theoretical results in the following table.

[12] C. M. HARRIS, B. F. HOSKINS and R. L. MARTIN, *J. Chem. Soc.* 3728 (1959).

(2) *Absorption spectra*

Spectra were determined on a Unicam SP500 spectrophotometer. Chloroform used as solvent was kept over anhydrous potassium carbonate to remove water and hydrochloric acid. Gaussian analyses were made by trial and error.

Cupric alkanoate–alkanoic acid solutions were examined at copper concentrations of 10^{-3} g-atom/l. and alkanoic acid concentrations of 5×10^{-2} mole/l.; pyridine complexes were examined in solutions

Compound	% Cu found	Formula	% Cu required
Acetate anhydrous	34·7	$(CH_3COO)_2Cu$	34·9
Acetate hydrate	31·4	$(CH_3COO)_2Cu \cdot H_2O$	31·8
Propionate anhydrous	30·0	$(C_2H_5COO)_2Cu$	30·2
Propionate hydrate	27·4	$(C_2H_5COO)_2Cu \cdot H_2O$	27·8
n-Butyrate hydrate	24·9	$(C_3H_7COO)_2Cu \cdot H_2O$	24·8
Isobutyrate anhydrous	26·9	$(C_3H_7COO)_2Cu$	26·7
Isobutyrate hydrate	25·1	$(C_3H_7COO)_2Cu \cdot H_2O$	24·8
n-Valerate hydrate	22·0	$(C_4H_9COO)_2Cu \cdot H_2O$	22·3
Pivalate hydrate	22·4	$(C_4H_9COO)_2Cu \cdot H_2O$	22·3
Caproate hydrate	20·1	$(C_5H_{11}COO)_2Cu \cdot H_2O$	20·3
Octoate anhydrous	17·8	$(C_7H_{15}COO)_2Cu$	18·2
Octoate hydrate	17·1	$(C_7H_{15}COO)_2Cu \cdot H_2O$	17·3
β-Chloropropionate hydrate	21·1	$(ClC_2H_4COO)_2Cu \cdot H_2O$	21·3
Phenylacetate anhydrous	18·9	$(C_7H_7COO)_2Cu$	19·0
β-Phenylpropionate anhydrous	17·7	$(C_8H_9COO)_2Cu$	17·6
Crotonate anhydrous	27·4	$(C_3H_5COO)_2Cu$	27·2

of copper concentration 10^{-3} g-atom/l., free alkanoic acid concentration 5×10^{-2} mole/l. and pyridine concentration 5×10^{-2} mole/l. These solutions obey Beer's law over very wide ranges of dilution. Dioxane complexes were examined in solutions of copper concentration 10^{-3} g-atom/l., alkanoic acid concentration 10^{-3} mole/l. and dioxane concentration 1·0 mole/l.; these solutions obey Beer's law only when a large excess of dioxane is present and the concentration of alkanoic acid is low.

Absorption spectra of solutions of the hydrated cupric alkanoates in chloroform were determined at the following concentrations of copper: propionate 0·0040, isobutyrate 0·0013, pivalate 0·0025, n-octoate 0·0025 and β-chloropropionate 0·0038 g-atom/l. 4 cm cells were used throughout in the ligand-field region and 0·1 or 0·2 cm cells in the charge–transfer region.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 232 to 239. Pergamon Press Ltd. Printed in Northern Ireland

THE ELECTRODEPOSITION OF INSOLUBLE HYDROXIDES —AN EXPERIMENTAL INVESTIGATION

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(*Received* 25 *May* 1960)

Abstract—The cathodic deposition of radioactive rare earths has been studied. The experiments establish the existence of a critical current density I_{min}, below which no deposition takes place. The dependence of I_{min} on the acid concentration and the stirring rate was examined for nitric acid solutions. The results are in agreement with calculations based on the diffusion layer concept. The addition of inert salts such as $Ba(NO_3)_2$ or KNO_3 causes a substantial decrease in the deposition rate. Most experiments have been performed with platinum cathodes, but silver and gold are equally applicable. Alcohol in the solution improves the source quality.

IN a previous paper[1] it was pointed out that the cathodic deposition of insoluble hydroxides can be treated as a process governed by the diffusion of hydrogen and hydroxyl ions in a diffusion layer attaching to the surface of the electrode. The following results were derived from the diffusion equations, which are valid in the presence of an inert salt.

(a) Deposition can be expected to take place only if

$$Il > D_H C \tag{1}$$

I denotes the current density, l the diffusion layer thickness, D_H is the diffusion coefficient for the hydrogen ion and C is the hydrogen ion concentration in the solution. If C is considered fixed, this inequality defines a minimum current density.

(b) A hydroxyl ion layer of thickness

$$l_{OH} = l - D_H C/I \tag{2}$$

attaches to the cathode.

(c) If condition (a) is fulfilled the hydrogen ion concentration at the cathode surface can be expressed as

$$c_H = \frac{D_{OH} K_W}{Il - D_H C} \tag{3}$$

Reference 1 contains references to a number of papers dealing with the procedures for the electrodeposition of insoluble hydroxides. Relatively little information, however, is available on the deposition parameters. It was therefore felt that such an investigation could be of interest, both in order to test the applicability of the hypotheses summarized above and in order to provide data that could be used in the planning of experiments utilizing this technique.

1. EXPERIMENTAL PROCEDURE

The cell used in most of the experiments is shown in Fig. 1. It is in principle similar to the one

[1] P. G. HANSEN, *J. Inorg. Nucl. Chem.* **12**, 30 (1959).

described by JOLIOT[2]. A relatively thin (20 mg/cm²) platinum window was used as the cathode. The radioactive deposit formed on the cathode was measured continuously by means of a Geiger counter connected to a count-rate meter. Before each experiment the foil was cleaned with hot nitric acid and hot hydrochloric acid followed by a wash with alcohol and ether.

Radioactive thulium was chosen as the tracer for experiments with this cell. ^{170}Tm formed by neutron capture in natural Tm is well suited for the purpose since the 0·97 MeV β-group is easy to detect, and since the decay is followed only by X-rays and γ-rays of low intensity. ^{170}Tm in the solution contributed little to the background of the Geiger counter. 31 μg Tm, corresponding to approximately 5 μC were added to the cell in each experiment.

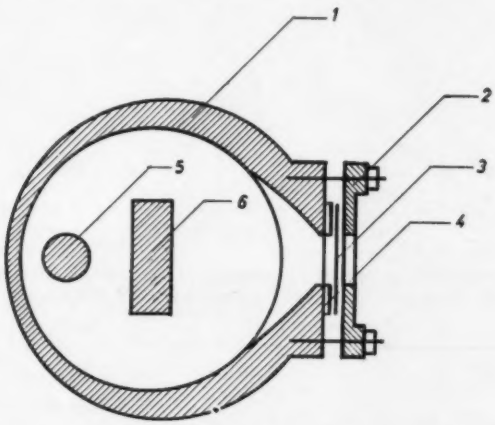

FIG. 1.—Horizontal cross-section through the electrodeposition cell. The inner diameter is 4·0 cm and the cathode area is 0·50 cm². The volume of solution in the cell is 40 ml. 1: Lucite cell, 2: Brass holder, 3: Platinum foil, 4: Rubber gasket, 5: Anode, 6: Stirrer.

The solutions were made up from double distilled water and reagent grade chemicals. The deposition curve was usually followed for 20 min. Since the deposit dissolves quantitatively when the current is turned off, experiments involving the same conditions in the liquid could be carried out without changing the solution.

The accuracy of such measurements appears to be limited. On several occasions sudden "drops" in the deposition curves were observed—an event that could only be explained as a release of activity from the cathodic deposit. Furthermore the marked dependence on the stirring rate (see Section 2.1) formed an appreciable contribution to the experimental error in addition to the systematic effect of stirring due to the hydrogen evolution.

2. EXPERIMENTAL RESULTS

The experimental arrangement shown in Fig. 1 was used in all experiments except those described under 2.5, 2.6 and 2.7.

2.1 *Critical current density.* It was borne out by a large number of experiments, that the concept of a critical current density is applicable to the cathodic deposition of insoluble hydroxides from acid solutions. As an example Fig. 2A shows the deposition curves obtained from 0·01 M HNO_3. Fig. 2B shows the amount deposited after 20 min as a function of the current density. The curve clearly shows the existence of a critical current density.

From the arguments outlined above it could be expected that I_{min} should be proportional to C, the hydrogen ion concentration in the solution, and inversely proportional to l, the thickness of the diffusion layer. The results of a series of measurements

[2] F. JOLIOT, *J. Chim. Phys.* **27**, 119 (1930).

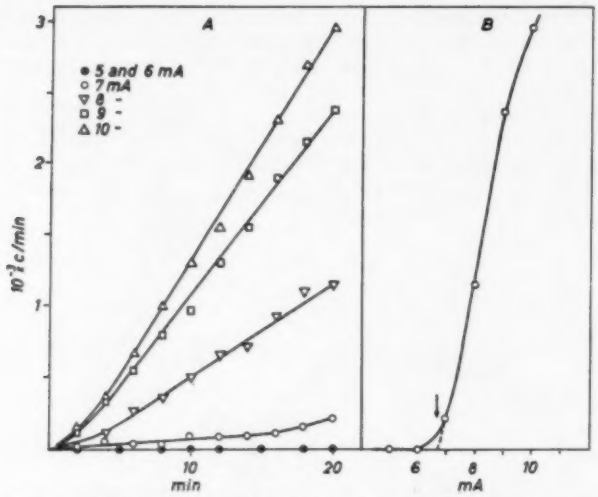

FIG. 2.—Deposition of thulium from 0·01 M nitric acid. Stirring rate 17 rev/sec. A. Activity deposited as a function of time, B. Activity deposited after 20 min as a function of current.

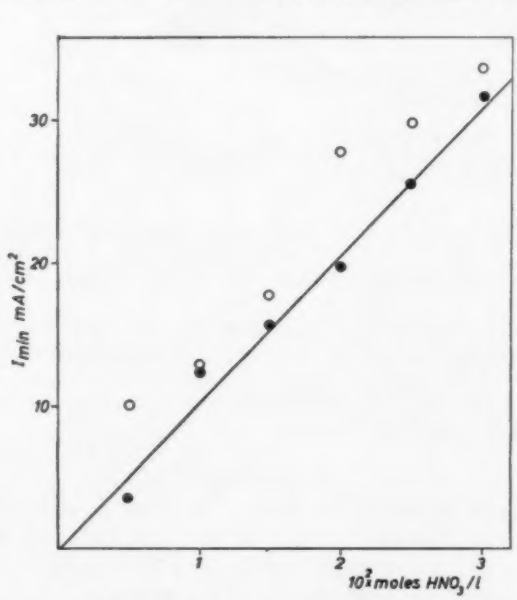

FIG. 3.—Critical current density for varying concentrations of nitric acid. Stirring rate 17 rev/sec. Black dots correspond to a solution 0·03 M in potassium nitrate, open dots refer to experiments with acid alone.

with varying C are summarized in Fig. 3. It is seen that I_{min} is approximately proportional to the hydrogen ion concentration. From the straight line (corresponding to the black dots) a value for D_H/l can be computed. Assuming that $D_H = 9{\cdot}0 \times 10^{-5}$ cm²/sec, one obtains $l = 0{\cdot}008$ cm. This result is slightly higher than the values normally found; the cathode arrangement used here could, however, be expected to make

the stirring less efficient. It is seen that the critical current densities are not much different in acid alone and in acid plus 0·03 M KNO_3. In view of the pronounced effect on the deposition rate of salt addition (see Section 2.2) it was felt that similar experiments carried out in a 'constant salt medium' would be of limited practical interest (see Section 4 'Conclusion'). In the concentration range investigated here I_{min} appears to be almost independent of salt concentration.

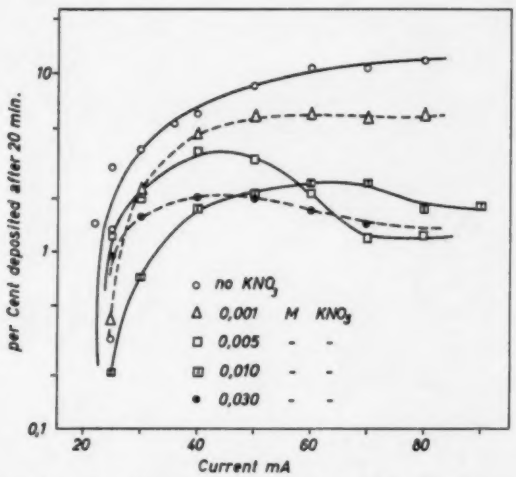

FIG. 4.—Deposition of thulium from 0·03 M nitric acid containing varying amounts of potassium nitrate. Stirring rate 17 rev/sec.

The dependence of I_{min} on l was tested by means of varying the stirring rate. In 0·03 M HNO_3 the critical current density was 16 mA/cm² at a stirring rate of about 6 rev/sec. At 17 rev/sec the result was 40 mA/cm². The result is qualitatively in agreement with the decrease in l, that could be expected from the increased stirring rate.

2.2 *Salt addition.* It has been found[3] that the addition of inert salts diminishes the deposition rate. This effect was also observed in the present investigation, and under the experimental conditions used here it was considerably more pronounced. A few typical curves showing the effect of salt addition are given in Fig. 4.

A cross-section through the data on salt effects is given in Fig. 5. It is seen that the effect of ammonium nitrate is almost negligible, whereas with barium nitrate and potassium nitrate the deposition rate decreases rapidly at concentrations around 10^{-3} M and levels off at higher concentrations. Experiments were performed with sulphuric acid solutions containing varying amounts of potassium sulphate. The results were very similar to those obtained with nitric acid containing barium or potassium nitrate.

2.3 *Deposition from various acids.* Fig. 6 shows the percentages deposited after 20 min from various solutions. It is seen that no essential differences exist between the deposition rates obtained from strong inorganic acids and those obtained from weak organic acids.

2.4 *Dissolution rate.* It is a general feature in the electrodeposition of hydroxides from acid solutions that the precipitate will redissolve when the current is turned off.

[3] G. LANGE, G. HERRMANN and F. STRASSMANN, *J. Inorg. Nucl. Chem.* **4**, 146 (1957).

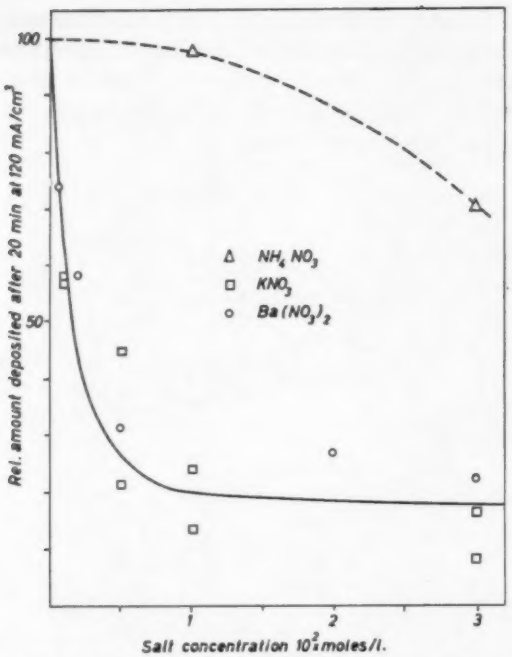

FIG. 5.—Relative deposition rate from 0·03 M nitric acid as a function of salt molarity.

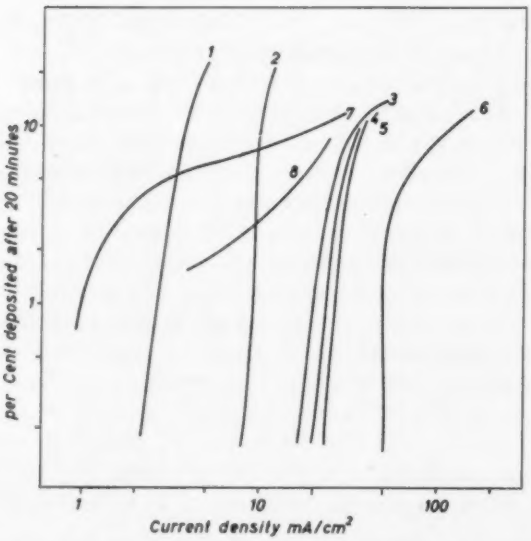

FIG. 6.—Deposition rate from various acids as a function of current density. 1: 0·01 M acetic acid, 2: 0·01 M formic acid, 3: 0·01 M nitric acid, 4: 0·01 M hydrochloric acid, 5: 0·005 M sulphuric acid, 6: 0·03 M nitric acid, 7: 0·01 M ammonium nitrate, 8: 0·01 M ammonium formate.

This difficulty can be circumvented by removing the cathode from the solution with the voltage on[3] or by adjusting the solution to an alkaline pH before interruption of the current.[4] As a guide for the evaluation of dissolution effects the results of some measurements are given in Table 1.

2.5 *Cathode materials.* Gold and silver were tested as cathode materials using a 6 ml cell with a 1·5 cm^2 cathode. The deposition rates were not significantly different from the rate obtained with a platinum cathode. From 0·01 M HNO_3 approximately 98 per cent ^{147}Pm was deposited in two hours at 50 mA.

2.6 *Alcohol addition.* The use of nonaqueous solvents, either alone or in conjunction with water, has often been reported in the literature (see e.g. refs. 5 and 6). It was

TABLE 1.—TIME FROM CURRENT TURNED OFF UNTIL 75 PER CENT OF THE ACTIVITY WAS DISSOLVED. STIRRING RATE: 17 rev/sec

Solution	Time
3×10^{-2} M HNO_3	5–10 sec
10^{-2} M HCOOH	20 sec
10^{-2} M CH_3COOH	65 sec
10^{-2} M NH_4NO_3	2·7 min
10^{-2} M $HCOONH_4$	160 min

therefore felt worthwhile to examine this technique. Alcohol was chosen as an exponent of the nonaqueous media, and experiments were performed with 0·01 M nitric acid in a 85 per cent alcohol–15 per cent water solution. No change in deposition rate was observed as compared 0·01 M nitric acid in water at the same current density. Nevertheless certain advantages pertain to the use of alcoholic media. It has been reported[6] that macroscopic deposits formed cathodically from alcohol–acetone solutions are more adherent than those formed from aqueous solutions. In the present investigation autoradiographs of ^{147}Pm deposits showed that those obtained from alcoholic media were more uniform than those obtained from aqueous solutions. The effect should be useful where very uniform deposits are desired.

2.7 *Dimensions of apparatus.* All other parameters kept constant, the amount deposited $N(t)$ at time t can be expected to depend on cell volume V and cathode area A in the following manner $N(t)/N(\infty) = [1 - \exp(-kAt/V)]$, if one assumes the process to follow a first order law.[6] This relationship was found to be approximately true in experiments where platinum wires differing in length were used as cathodes, while current density and stirring rate were kept constant.

3. DISCUSSION

Evidence for the existence of pH-gradients in the vicinity of a cathode is also available from the study of concentration overvoltage at hydrogen electrodes. Calculations

[4] W. G. SMITH, UCRL–2974 (1955).
[5] S. COTELLE and M. HAISSINSKY, *C. R. Acad. Sci., Paris* **206**, 1644 (1938).
[6] V. B. DEDOV and V. N. KOSYAKOV, *Proceedings of the 1st International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, Vol. 7, P. 369. United Nations, New York (1956).

on the magnitude of this effect have been performed by KING[7], who derived an equation identical to (3). In a study of concentration polarization in acid solutions (0·2 M HCl–2·0 M KCl), COATES[8] found a sharp increase in the overvoltage–current density curve corresponding to the limiting current (0·3 A/cm^2). Current densities higher than this could be obtained, the concentration overvoltage rising only slowly from a value about 0·8 V. This was interpreted as indicating the formation of an alkaline layer at the cathode, an assumption that was confirmed by adding a magnesium salt to the solution. The concentration overvoltage then remained constant at a value corresponding to the solubility product of magnesium hydroxide.

COATES futhermore observed that the limiting current could be exceeded even in solutions of pure acids. The concentration overvoltage measured in this case was again of the order of 0·8 V. The possibility that pH could rise above seven was ruled out from electro-neutrality considerations, and COATES therefore explained the overpotential in terms of a slight electrical unbalance close to the cathode giving rise to a double layer potential. The limiting current density was found to be a factor six lower in the presence of an inert salt than it was in acid alone—a result that was ascribed to the change in transference number for the hydrogen ion.

For solutions containing acid and an inert salt the conditions (though not the mechanism) for hydroxide deposition are relatively clear. The critical current density can be measured radiochemically and has been shown to correspond to the formula (1). An effect that may be due to the thickness of the hydroxyl ion layer, defined in (2), can be seen in Fig. 4. At the higher salt concentrations the deposition rate reaches a maximum, and then decreases with increasing current density. Similar curves were obtained with barium nitrate and potassium sulphate solutions. It seems likely that the decrease in deposition rate is correlated with the increasing thickness of the hydroxyl ion layer. The high pH value at the cathode predicted by equation (3) can be measured directly by electrochemical techniques, as was shown by COATES.

For solutions containing acid alone the results obtained deserve special consideration, firstly because this method obviously is the method of choice in practical applications, and secondly because the diffusion treatment outlined in the beginning of this paper is not applicable here. The critical current density must now be determined by the combined diffusion and electromigration of the hydrogen ions, and furthermore a hydroxyl ion layer of thickness comparable to l cannot exist. In the range of salt concentrations studied in the present investigation the critical current density was found to be almost independent of salt concentration. It is interesting to note the pronounced similarity of the overvoltage–current density curves (in the measurements made by COATES) for solutions containing inert salts and for salt free solutions. This similarity may of course be accidental, as the deposition conditions are not obvious in solutions of acid alone. Combining this similarity with the fact that hydroxide deposition does take place from pure acids, it is, however, natural to assume that a very thin alkaline layer attaches to the cathode giving rise to a double layer potential of the type described by COATES and to a concentration overpotential. The increased deposition rate in acid alone is probably related to the fact that the deposit can form only very close to the cathode—a feature that could be expected to have a marked influence on the 'sticking probability' of the hydroxide precipitate.

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4. CONCLUSION

The experimental results demonstrate the existence of a critical current density that can be calculated from the inequality (1). The deposition rate decreases considerably when inert salts are present and deposition from acid alone is therefore preferable. Under these circumstances the deposition rate increases with current density. As the gas evolution at the electrodes generally is a drawback to this procedure because of radioactive spray, it is usually advantageous to use a weak acid as the solvent. Platinum, gold and silver are equally applicable as cathode materials, and, as usual in electro-deposition work, a high ratio of electrode area to cell volume is desirable. The addition of alcohol to the solution has been found to improve the source quality.

Acknowledgement—The author is indebted to Mrs. J. HØGH for skilled technical assistance.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 240 to 243. Pergamon Press Ltd. Printed in Northern Ireland

ON THE RESOLVABILITY OF THE TRIS(CATECHOLATO) ALUMINATE ION

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(*Received* 13 *June* 1960; *in revised form* 5 *July* 1960)

Abstract—Repeated attempts to resolve the *tris*(catecholato) aluminate ion using reported procedures were uniformly unsuccessful. All instances where rotations were observed could be attributed to residual resolving agent. An examination of the ligand exchange with 4-chlorocatechol shows that such exchange is rapid at a pH of 8·6 at 25°C. In contrast to this, the residual optical activity observed with solutions in which the presumably resolved complex was present showed no noticeable change over a period of days.

ONE of the most direct and effective chemical methods of establishing the octahedral structures of hexacoordinate atoms is through the resolution of suitable asymmetric complexes.

This particular method has been used in the study of complexes of many hexa-co-ordinated central ions including Al(III).[1-4]

Reports of the resolution of $[Al(C_2O_4)_3]^{3-}$ were followed by conflicting opinions on the validity of these reports. Recent attempts to resolve this ion at −35°C by preferential abosrption on starch were unsuccessful.[5] Thus the tris(oxalato) aluminate(III) ion was reputedly resolved by fractional crystallization of the cinchonine salt, although the literature[1,2] on this particular point is rather discordant. Information on the Al—O bonds in this complex was provided by subsequent work of LONG[6] who showed that the exchange of labelled (C″) oxalate with the complex was essentially complete in 20 sec at 35°C.

The present work is concerned with the closely related problem of the resolution of the tris(catecholato) aluminate(III) ion. Salts of this anion were first prepared by WEINLAND[7]. Subsequently, its resolution was reported by TREADWELL and his co-workers.[3] The separation of the diastereoisomers with L-strychnine was reported to be effected through their differences in solubility in cold water. The salt with the L-enantiomorph was claimed to be less soluble than that of the D-enantiomorph. The isolation of the latter form was not claimed. We have examined this resolution process in considerable detail as well as the exchange of the complex with 4-chlorocatechol. Our results differ significantly from those reported earlier on this complex, but are consistent with the known behaviour of the oxalato complex.

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EXPERIMENTAL

(a) *Preparation of ammonium tris(catecholato)aluminate(III)*

The apparatus of Fig. 1 was employed in the preparation of this complex. This compound is best prepared in an inert atmosphere, since basic solutions of catechol react extremely rapidly with atmospheric oxygen to give greenish-black solutions.

Three-tenths of a mole of catechol (33 g) was mixed with one-tenth mole of aluminum nitrate (37·5 g of $Al(NO_3)_3 \cdot 9H_2O$) in flask A and thoroughly mixed in the dry state by use of the magnetic stirrer. The apparatus was then thoroughly flushed with nitrogen to expel all air and a slow stream of nitrogen was continued throughout the experiment. Air-free distilled water (250 ml) was added to

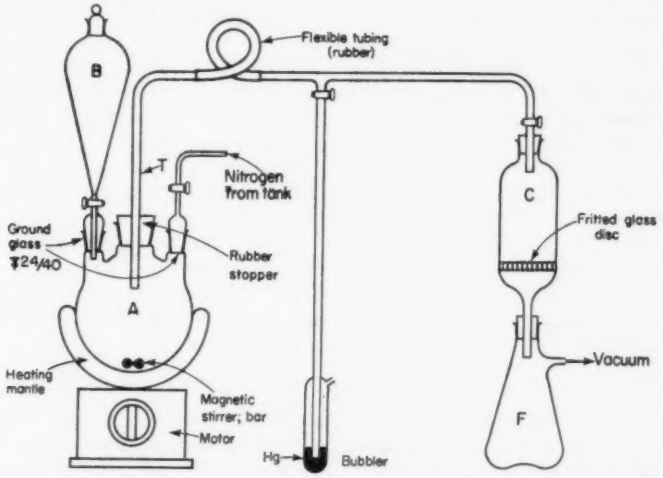

FIG. 1.—Apparatus used in the preparation of the ammonium and potassium salts of the tris(catecholato)aluminate(III) ion.

flask A via the tap funnel B and the contents heated almost to boiling with continuous stirring. After heating for about five minutes, 40 ml of concentrated ammonia solution ($d = 0{\cdot}90$) dissolved in 100 ml of air-free distilled water was added slowly through the tap funnel B, making certain that no air enters the apparatus. After this addition, the solution is cooled in an ice-bath, upon which fine needles of the ammonium salt crystallize from the solution. The tube T is then pushed down through the lubricated rubber stopper until it reaches the bottom of the flask A. Application of vacuum to filter flask F then draws the product over and into the filtration flask C. The crystals obtained here are washed with three 100 ml portions of acetone (added via the tap funnel B) and then sucked dry under nitrogen. The product may be recrystallized from aqueous methanol, taking care not to boil the solution since decomposition occurs under these conditions with the resulting evolution of ammonia and rapid darkening of the solution due to oxidation. Previous reports stated that this salt is stable to boiling. The product was dried in a vacuum dessicator over magnesium perchlorate. Analysis of the product showed the composition to be intermediate between that of the anhydrous salt and that of the sesqui hydrate. Attempts to prepare the anhydrous compound resulted in a loss of ammonia and subsequent decomposition.

(b) *Conversion of the ammonium salt to the potassium salt*

Forty grams (0·1 mole) of the ammonium salt was treated with a solution of 18 g (0·3 mole) of potassium hydroxide in 50 ml of distilled water and refluxed gently under nitrogen until no further evolution of ammonia was detectable. Water was removed under vacuum until crystallization commenced, the mixture was cooled to 0°C, and the product filtered off and washed with acetone. Drying was accomplished by heating to 100°C. at 5 mm for 4–6 hr and did not result in the decomposition of the potassium salt. The product may be purified by precipitation from aqueous solution by addition of acetone or by recrystallization from dimethylformamide. Due to the much greater solubility of the potassium salt in water, it could not be prepared readily in the same manner as the

ammonium salt. However, the use of freshly precipitated and washed aluminium hydroxide in place of aluminium nitrate reduces the water content of the system sufficiently to allow the potassium salt to be prepared by a method analogous to that used for the ammonium salt. The anhydrous potassium salt is $K_3[Al(C_6H_4O_2)_3]$. (Found: K, 24·7, Al, 5·70, Catechol, 69·0. Calc. for $K_3[Al(C_6H_4O_2)_3]$: K, 24·9 Al, 5·76, Catechol (as $C_6H_6O_2$), 68·8%). Potassium was determined gravimetrically as the tetraphenyl borate[8] after decomposing the organic matter with concentrated nitric acid. Aluminium was determined gravimetrically as the oxinate[9] after similar removal of the organic matter. Catechol was determined volumetrically by the method of PENCE[10].

(c) *Attempted resolution*

The procedure reported by TREADWELL *et al.*[3] was utilized and the rotatory power of the various fractions was determined using a Schmidt and Haensch polarimeter reading to 0·01°. All readings were made at 25° using the yellow Na *D* line and a 2 dm tube. This yellow Na *D* line was also used by TREADWELL *et al.* Repeated attempts failed to show any change in the rotatory power of the solutions with time, as would be expected for an enantiomorph capable of racemization. The only rotations observed were those due to the L-strychnine used as the resolving agent. These rotations agreed in sign and magnitude with those attributed earlier to the aluminium complex. Furthermore, no trace of the D-complex (reputedly more soluble in cold water) could be found, though frequent attempts were made to obtain evidence for such a species through measurements of the rotatory powers of the solutions. In all cases, the only rotations observed were due to the L-strychnine and were *invariant* with time. A solution of the presumably resolved complex in acetic acid showed the same rotatory power as in basic aqueous solution. The only species in the system which could exhibit such behaviour was the resolving agent itself. The brucine salt of the complex anion was also prepared. All attempts at resolution through this salt also failed.

(d) *Exchange of* $K_3[Al(C_6H_4O_2)_3]$ *with 4-chlorocatechol*

Ten millilitres of an approximately 0·1 M solution of $K_3[Al(C_6H_4O_2)_3]$ in air-free distilled water was mixed rapidly with 10 ml of an approximately 0·3 M solution of 4-chlorocatechol, also in air-free distilled water. The mixture was shaken and allowed to stand 5 min in a bath thermostated at 25°C while a slow stream of nitrogen was passed through the reaction flask. At the end of 5 min the reaction was stopped by the precipitation of the complex anion. This was accomplished by the addition of 5 ml of a 20 per cent solution of pyridine nitrate. The precipitate was collected on a fritted glass crucible and washed with water. The whole of the precipitate was then dissolved in 50% HNO_3. The resulting solution was then rendered slightly basic with 3 M KOH and then a 10 ml excess of 3 M KOH was added. Hydrogen peroxide (30 per cent) was then added in small portions and the solution was heated with further additions of small portions (2 ml) of hydrogen peroxide until a clear solution was obtained (about 30–45 min were required). The total chloride in this solution was then determined by a Volhard titration. Blank runs showed that no precipitate was obtained when only catechol and pyridine nitrate were present under similar circumstances. A set of similar experiments were run using the hexamminecobalt(III) ion as the precipitant for the complex anion. The 4-chlorocatechol was obtained from K and K Labs Inc. N.Y. and was recrystallized to obtain a white crystalline solid m.p. 87–88° uncorr. (Beilstein gives 84–85°). Two typical runs are summarized below:

Temperature, 25°C; pH = 8·6; Time of Reaction, 5 min:

Concentration of $K_3[Al(C_6H_4O_2)_3]$	4-Chlorocatechol	Cl^- taken up by complex	Exchange ratio†	Precipitant
0·1 M	0·3 M	0·1036	0·45	$Co(NH_3)_6^{3+}$
0·099 M	0·299 M	0·1118	0·53	Pyridine nitrate*

* The pH of the pyridine nitrate solution was adjusted to 7.

† The exchange ratio is defined as $y \Big/ \left[x - y\left(\frac{110}{145}\right) \right]$ where x is the number of grammes of pure catechol originally present in the complex and y is the number of grammes of halogenated ligand present after exchange.

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[10] C. M. PENCE, *J. Industr. Engng. Chem.* **5**, 218 (1913).

The gross exchange of 4-chlorocatechol for catechol in the complex anion $[Al(C_6H_4O_2)_3]^{3-}$ in basic solution is thus quite rapid. The fact that the halogenated ligand can appear in co-ordination with the aluminium after such a short time indicates that the complex anion is quite labile in solution.

In conclusion, the failure to reproduce the reported resolution and the rapid exchange with the substituted ligand support the view that the tris(catecholato) aluminate(III) ion, like the tris(oxalato) aluminate(III) species, is sufficiently unstable to defy resolution by classical chemical methods.

Acknowledgement—This work was supported by the U.S. Atomic Energy Commission.

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J. Inorg. Nucl. Chem. 1961, Vol. 17, pp. 244 to 247. Pergamon Press Ltd. Printed in Northern Ireland

INTERACTION OF PLATINUM (II) AND PLATINUM (IV) WITH 1,2,3-BENZOTRIAZOLE

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(*Received* 6 *September* 1960)

Abstract—As part of a systematic study of the interaction of the platinum elements with 1,2,3-benzotriazole, this paper presents methods for the synthesis of several 1,2,3-benzotriazole co-ordination compounds of platinum. Also reported are several 1,2,3-benzotriazole co-ordination compounds of platinum with certain halides in varying yields and high purity.

To pursue further the chemistry of the interaction of the platinum group elements with 1,2,3-benzotriazole, this study was undertaken to prepare co-ordination compounds of platinum through the interaction of platinum (II) and platinum (IV) with 1,2,3-benzotriazole under various conditions, to investigate the completeness of precipitation, and to determine the reproducibility and stoichemistry of the reactions.

In previous studies information concerning the reactions of the platinum group elements, viz., osmium, palladium and rhodium with 1,2,3-benzotriazole has been reported.[1–3]

EXPERIMENTAL

Apparatus and materials. The pH meter employed in this study was a Beckman Zeromatic pH meter model 96. The metal determinations were carried out in an open Hoskins Electric Furnace in which the compounds were decomposed to free platinum in platinum crucibles. All precipitates were filtered using medium porosity sintered-glass crucibles.

Reagents and preparation of solutions. A 2·5% aqueous solution of 1,2,3-benzotriazole was prepared from a weighed amount of 1,2,3-benzotriazole, Eastman Kodak Chemical No. 2759, that had been recrystallized twice from chloroform. The pH of a 2·5% aqueous solution of 1,2,3-benzotriazole is approximately 7.

The stock solution of potassium tetrachloroplatinate (II) and potassium hexachloroplatinate (IV) were prepared by dissolving a 1 g sample of each in separate 150 ml beakers containing 50 ml of water and enough concentrated hydrochloric acid per beaker to produce a solution of pH 1. The partially dissolved substances were warmed several minutes on a steam bath to complete dissolution. The resulting solutions of potassium tetrachloroplatinate (II) and of potassium hexachloroplatinate (IV) were then filtered into a 250 and 500 ml volumetric flask, respectively, and diluted to volume with distilled water which had been adjusted to a pH of 1.

The platinum (IV) chloride solution was prepared by dissolving a 1 g sample of platinum tetrachloride in 10 ml of concentrated hydrochloric acid and diluting with distilled water until the solution indicated a pH value of 1. The solution was then filtered into a 500 ml volumetric flask and diluted to volume with water of the same pH.

The platinum (IV) bromide stock solution was prepared by dissolving a 1 g sample of platinum (IV) bromide in 15 ml of 32% hydrobromic acid solution, and the resulting solution was adjusted to a pH of 1 with distilled water. After filtering the solution into a 500 ml volumetric flask, the solution was diluted to volume using distilled water of pH 1.

[1] R. F. WILSON and L. E. WILSON, *J. Amer. Chem. Soc.* **77**, 6204 (1955).
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The platinum (IV) iodide stock solution was prepared by partially dissolving 1 g of the reagent in 25 ml of 47% hydroiodic acid. After addition of approximately 800 ml of distilled water, the mixture was warmed several minutes on a steam bath until complete dissolution had taken place. The solution after being cooled to room temperature was adjusted to a pH of 1 and then diluted to volume in a litre volumetric flask with water of the same pH.

Each of the aforementioned stock solutions was later modified as needed by varying the pH using concentrated solutions of sodium acetate or sodium bicarbonate.

All chemicals used in this study were reagent grade. The platinum metal compounds were obtained from A. M. Mackay, Inc.

Analytical method. The platinum content in the compounds reported was determined by decomposing the products in an electric furnace. The remaining metal was weighed directly. Carbon, Hydrogen, Nitrogen and the Halogens were determined using conventional methods of analysis. The results were checked by the Laboratory of Microchemistry, Teaneck, New Jersey.

Preparation of $Pt(C_6H_4NHN_2)_3(C_6H_4N_2N)Cl$, *a greenish white compound.* Three 50 ml aliquots of potassium tetrachloroplatinate (II) solution of pH 1 containing $1{\cdot}880 \times 10^{-3}$ g of platinum per ml of solution were introduced into 125 ml. Erlenmeyer flasks, each containing 50 ml of the 2·5% 1,2,3-benzotriazole solution. The pH of the resulting solution was approximately 1. After addition of the potassium tetrachloroplatinate (II) solution, a white precipitate began to form. The mixtures were digested for 1 hr on a steam bath, then the precipitates, while hot, were collected on medium porosity sintered-glass crucibles. The precipitates were washed with several aliquots of hot water, the total volume being 150 ml, dried in a vacuum desiccator over magnesium perchlorate for 24 hr, and weighed. The weights of the precipitates were 320·84, 319·90 and 319·60 mg. Average yield: 94·1%. (Found: Pt, 27·66; C, 41·05; N, 23·62; H, 2·70; Cl, 4·84. Calc. for $Pt(C_7H_4NHN_2)_3(C_6H_4NN_2)Cl$: Pt, 27·63; C, 40·83; N, 23·81; H, 2·71; Cl, 5·02%). The probable reaction at a pH of approximately 1 is

$$PtCl_4^{=} + 4C_6H_4NHN_2 \rightarrow Pt(C_6H_4NHN_2)_3(C_6H_4NN_2)Cl + H^+ + 3Cl^-.$$

Preparation of $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_2$, *a white compound.* The potassium chloroplatinate (II) stock solution was modified by changing the pH value from 1 to a pH value of 6·5 with a concentrated solution of sodium acetate. Three 50 ml aliquots of potassium chloroplatinate (II) stock solution of pH 6·5 were introduced into 125 ml Erlenmeyer flasks containing 50 ml each of 2·5% 1,2,3-benzotriazole solution. No precipitation occurred at room temperature; however, after 15 min of digestion a precipitate began to form. The mixtures were digested on a steam bath for 1 hr and the precipitates were collected, washed, dried, and weighed. The weights of these precipitates were 319·40, 318·22 and 318·61 mg. Average yield: 98·8%. (Found: Pt, 29·21; C, 42·78; N, 25·37; H, 2·76. Calc. for $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_2$: Pt, 29·14; C, 43·05; N, 25·10; H, 2·71%). The reaction at a pH of 6·5 is indicated as follows

$$PtCl_4^{=} + 4C_6H_4NHN_2 \rightarrow Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_2 + 2H^+ + 4Cl^-.$$

Preparation of $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_3Cl$, *a yellow coloured compound.* Three 50 ml aliquots of the potassium hexachloroplatinate (IV) solution containing $8{\cdot}028 \times 10^{-4}$ g of platinum per ml of solution were introduced into 125 ml Erlenmeyer flasks containing 50 ml each of 1,2,3-benzotriazole stock solution. To expedite the precipitation, the mixtures were digested on a steam bath for 45 min. At the completion of the digestion period, a bright yellow precipitate had developed. The precipitates were collected, washed, dried, and weighed. The weights of the precipitates were 155·23, 154·84 and 155·40 mg. Average yield: 91·7%. (Found: Pt, 23·58; C, 43·50; N, 25·77; H, 2·52; Cl, 4·34. Calc. for $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_3Cl$: Pt, 23·70; C, 43·77; N, 25·53; H, 2·69; Cl, 4·31%). The reactions seem to follow the path

$$PtCl_6^{=} + 5C_6H_4NHN_2 \rightarrow Pt(C_6H_4NN_2)_2(C_6H_4NN_2)_2Cl + 3H^+ + 5Cl^-.$$

Preparation of $Pt(C_6H_4NHN_2)(C_6H_4NN_2)_4 \cdot H_2O$, *a greyish white compound.* Three 50 ml aliquots of potassium hexachloroplatinate (IV) solution of pH 6·7 were introduced into 125 ml Erlenmeyer flasks, each containing 50 ml of 2·5% 1,2,3-benzotriazole solution. The solutions were digested on a steam bath for 45 min. A fine granular precipitate developed; however, some of the hexachloroplatinate (IV) ion remained unreacted as indicated by the colour of the filtrate. The precipitates were

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collected, washed, dried, and weighed. The weights of the precipitates were 130·80, 131·20 and 131·40 mg. Average yield: 79·2%. (Found: Pt, 24·32; C, 44·79; N, 26·28; H, 2·69; Calc. for $Pt(C_6H_4NHN_2)(C_6H_4NN_2)_4 \cdot H_2O$: Pt, 24·24; C, 44·77; N, 26·11; H, 2·88%). The probable reaction is

$$PtCl_6^{=} + 5C_6H_4NHN_2 \rightarrow Pt(C_6H_4NHN_2)(C_6H_4NN_2)_4 \cdot H_2O + 4H^+ + 6Cl^-.$$

Preparation of $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_2Cl_2$, *a yellow coloured compound.* Three 50 ml aliquots of platinum tetrachloride solution of pH 1 containing $1{\cdot}158 \times 10^{-3}$ g of platinum per ml of solution were mixed with an equal volume of 2·5% 1,2,3-benzotriazole stock solution. Almost immediately a precipitate began to form. This reaction was allowed to proceed at room temperature for 24 hr. The precipitate was then collected, washed, dried, and weighed. The weights of the precipitates were 110·40, 113·01 and 112·71 mg. Average yield: 51·0%. (Found: Pt, 26·27; C, 38·70; N, 22·47; H, 2·29; Cl, 9·78. Calc. for $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_2Cl_2$: Pt, 26·35; C, 38·93; N, 22·70; H, 2·45; Cl, 9·58%). Elemental analyses indicated that the above compound could be produced at any pH over the pH range of 1 to 7. In the pH range of 1 to 7, the reaction appears to follow the path

$$PtCl_4 + 4C_6H_4NHN_2 \rightarrow Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)_2Cl_2 + 2H^+ + 2Cl^-.$$

Preparation of $Pt(C_6H_4NHN_2)(C_6H_4NN_2)I \cdot H_2O$, *a beige coloured compound.* Three 50 ml aliquots of the platinum tetraiodide stock solution containing $2{\cdot}776 \times 10^{-4}$ g of platinum per ml were mixed with equal volumes of 1,2,3-benzotriazole stock solution which gave a pH of approximately 1. The solutions were digested for 2 hr. As the precipitates formed, the iodine fumes could be seen escaping from solution. The resulting precipitates were collected, washed, dried, and weighed. The weights of the precipitates were 4·77, 4·68 and 4·70 mg. Average yield: 11·6%. (Found: Pt, 33·98, C, 24·67; N, 14·38; H, 1·78; I, 21·77. Calc. for $Pt(C_6H_4NHN_2)(C_6H_4NN_2)I \cdot H_2O$: Pt, 33·79; C, 24·96; N, 14·54; H, 1·92; I, 22·00%.) The data suggest the following reaction

$$PtI_4 + 2C_6H_4NHN_2 + H_2O \rightarrow Pt(C_6H_4NHN_2)(C_6H_4NN_2)I \cdot H_2O + H^+ + I^- + I_2.$$

Preparation of $Pt(C_6H_4NN_2)_2(H_2O)_2$, *a grey compound.* Three 50 ml aliquots of platinum tetraiodide stock solution of pH 6·0 were mixed with equal volumes of 1,2,3-benzotriazole stock solutions. The resulting solutions were digested for 2 hr. The precipitates were collected, washed, dried and weighed. The weights of these precipitates were 5·01, 5·03, 4·99 mg. Average yield: 15·1%. (Found: Pt, 41·65; C, 30·52; N, 17·77; H, 2·24; Calc. for $Pt(C_6H_4NN_2)_2(H_2O)_2$: Pt, 41·74; C, 30·84; N, 17·98; H, 2·58%). The reaction over the pH range of 4·5–7 can be represented as follows

$$PtI_4 + 2C_6H_4NHN_2 + 2H_2O \rightarrow Pt(C_6H_4NN_2)_2(H_2O)_2 + 2H^+ + 2I^- + I_2$$

Preparation of $Pt(C_6H_4NN_2)_3Br$, *an orange coloured compound.* Three 50 ml aliquots of platinum tetrabromide stock solution of pH 1 were added to equal volumes of 1,2,3-benzotriazole solution in 125 ml Erlenmeyer flasks. The stock solution of platinum tetrabromide contained $7{\cdot}580 \times 10^{-4}$ gm of platinum per ml of solution. Precipitation began almost immediately. The reaction was allowed to proceed at room temperature for 24 hr. The resulting precipitates were collected, washed, dried, and weighed. The weights of the precipitates were 10·98, 11·02 and 11·00 mg. Average yield: 9·0%. (Found: Pt, 30·89; C, 33·94; N, 20·37; H, 2·01; Br, 12·46. Calc. for $Pt(C_6H_4NN_2)_3Br$: Pt, 31·00; C, 34·35; N, 20·03; H, 1·92; Br, 12·70%.) The reaction seems to follow the path

$$PtBr_4 + 3(C_6H_4NHN_2) \rightarrow Pt(C_6H_4NN_2)_3Br + 3H^+ + 3Br^-.$$

Preparation of $Pt(C_6H_4NN_2)_4 \cdot Pt(C_6H_4NHN_2)(C_6H_4NN_2)_2$, *a beige compound.* Three 50 ml aliquots of the modified platinum tetrabromide solution of pH 6·0 were mixed with equal volumes of 1,2,3-benzotriazole stock solution. The solutions were digested for 1 hr on a steam bath. The precipitates were collected, washed, dried, and weighed. The weights of the precipitates were 15·25, 15·20 and 15·28 mg. Average yield: 12·9%. (Found: Pt, 31·90; C, 41·02; N, 24·37; H, 2·51. Calc. for $Pt(C_6H_4NN_2)_4 \cdot Pt(C_6H_4NHN_2)(C_6H_4NN_2)_2$: Pt, 32·03; C, 41·22; N, 24·15; H, 2·40%.) The path of the reaction is probably

$$2PtBr_4 + 7C_6H_4NHN_2 \rightarrow Pt(C_6H_4NN_2)_4 \cdot Pt(C_6H_4NHN_2)(C_6H_4NN_2)_2 + 6H^+ + 6Br^- + Brg.$$

DISCUSSION

While carrying out exploratory studies on the interaction of platinum (II) and platinum (IV) with 1,2,3-benzotriazole, gravimetric and elemental analysis data indicated that co-ordination compounds of constant composition could be obtained in neutral or nearly neutral media and in acidic media of 'pH 1 or lower'. The composition of most of the reaction products could be varied over the pH range of approximately 1–6·5. All of the compounds reported in this study were slightly soluble in water and in mineral acids. In no instance could any of the products obtained be precipitated from basic media. Moreover, the optimum acid pH range for precipitation of compounds of constant composition was obtained for each of the compounds.

In the interaction of potassium tetrachloroplatinate (II) with 1,2,3-benzotriazole over the pH range of 1–7, a compound of $Pt(C_6H_4NHN_2)_2(C_6H_4NN_2)Cl$ composition was obtained. From the interaction of platinum tetraiodide with 1,2,3-benzotriazole in acid media of pH 1, a compound of $Pt(C_6H_4NHN_2)(C_6H_4NN_2)\ I{\cdot}N_2O$ composition was produced. Whereas the same reactants in the pH range of 4·5–7 gave a compound of $Pt(C_6H_4NN_2)_2(H_2O)_2$ composition.

Further investigations of these compounds include plans for the application of magnetic susceptibility, thermogravimetric analysis, infra-red and X-ray studies for the purpose of elucidating the structures of these compounds.

Acknowledgement—The authors wish to express their sincere thanks to The Robert A. Welch Foundation for a grant, which supported this study.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 248 to 253. Pergamon Press Ltd. Printed in Northern Ireland

THE INTERACTION OF OSMIUM TETROXIDE AND AMMONIA*

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(*Received* 8 *August* 1960)

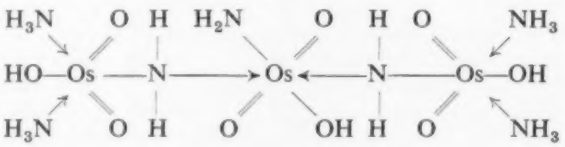
Abstract—The reaction between OsO_4 and either gaseous or liquid ammonia has been shown to involve reduction to Os^{6+} in a single osmium-containing product, $Os_3N_7O_9H_{21}$; the other products are nitrogen and water. Numerous properties of the osmium (VI) compound are described and a trinuclear structure that involves bridging through amido groups is suggested.

IT was observed by VASKA[1] that osmium tetroxide reacts with liquid ammonia to form a black solid which explodes violently when heated in gaseous ammonia at ca. 240°. The limited information available suggested that the reaction involved reduction of osmium (VIII) to osmium (VI).

The experimental data reported in this paper are the results of a quite detailed study of the reaction between osmium tetroxide and both gaseous and liquid ammonia. The experimental evidence is best understood with the *a priori* information that the reaction involved is represented by,

$$3OsO_4 + 9NH_3 \rightarrow Os_3N_7O_9H_{21} + N_2 + 3H_2O \qquad (1)$$

and that the constitution of the osmium-containing product that is most nearly compatible with all of the experimental data is,



EXPERIMENTAL

Reagent grade chemicals were used in all experiments. Osmium was determined by the method of GILCHRIST[2]; otherwise, standard methods of analysis were employed. X-ray diffraction patterns were obtained using CuK_α radiation (Ni filter) and a tube voltage and current of 35 kV and 15 mA, respectively; relative intensities were estimated visually. Infra-red spectra were obtained with a Baird recording spectrophotometer; both KBr disks and Nujol mulls were employed. Magnetic susceptibility measurements were made with a modified Curie-Cheneveau balance.[1]

General procedures

Because a very strongly exothermal reaction was involved, it was necessary to work with quantities of osmium tetroxide so small that localized heat of reaction would not raise the temperature of the reaction products to that at which explosions would occur. Consequently it was necessary first to carry out experiments to establish that the composition of the osmium-containing product was both

* This work was supported in part by the U.S. Atomic Energy Commission, Contract AT-(40-1)-1639, and by the Robert A. Welch Foundation.

[1] L. VASKA, Thesis, The University of Texas (1956).
[2] R. J. GILCHRIST, *J. Res. Nat. Bur. Standards* **6**, 421 (1931).

constant and reproducible, then to carry out separate experiments each of which usually provided only enough product for a particular kind of measurement.

The reactions were carried out in small all-glass vessels of low tare weight such that weights of solid reactants and products could be determined accurately. These vessels were connected to auxiliary lines that permitted evacuation of the reaction vessels, introduction of anhydrous ammonia, and the collection and analysis of gaseous reaction products. In some cases the OsO_4 was placed in the reaction vessel in fragile glass ampoules which, following evacuation, were broken with a magnetic hammer. Other procedures differed in that the ampoule was broken in a baffled side-arm and the OsO_4 was sublimed into the reaction vessel proper, so as to provide separation from glass fragments; thereafter the side-arm was sealed off while the main body of the reaction vessel was maintained at $-70°$.[3]

Typical experiment

A known weight of osmium tetroxide in a sealed glass ampoule was placed in the reaction vessel which was then maintained at a pressure of $<10^{-3}$ mm for 12 hr. The ampoule was broken and anhydrous ammonia gas was admitted until the pressure exceeded atmospheric pressure by 8 mm. Upon first contact with ammonia, the pale yellow crystals of the tetroxide assumed a bright orange colour. The intensity of the colour increased rapidly and after 5 min the solid appeared to melt. More ammonia was admitted at suitable time intervals (ca. 15 min) to maintain a positive pressure of 7–10 mm. After 30 min, the colour of the solid was brown and after 9 hr it was black. When there was no further evidence of reaction, the exit stopcock was opened and the vessel was swept out with anhydrous ammonia; water-insoluble gases were collected, measured and analysed. The reaction vessel was evacuated over night, opened in the dry-box, and the solid product was removed and analysed (see below). In some of these experiments the reaction vessel was removed at frequent intervals and weighed; the weight became essentially constant in 6 hr. The weights of OsO_4 (in moles $\times 10^3$) employed ranged from 1·30 to 12·82; the total time of contact of reactants ranged from 5 to 384 hr.

Other experiments differed only in that the anhydrous ammonia was delivered to the reaction vessel from a large gas burette in order to measure the quantity of ammonia consumed in the reaction or otherwise incorporated in the reaction products.

Composition of the solid product

The osmium content of three randomly selected samples of the black solid product from different experiments was found to be 68·8, 68·8 and 68·7 per cent. The total nitrogen content was similarly found to be 12·1, 11·9, and 12·0 per cent (calc. for $Os_3N_7O_9H_{21}$: Os, 68·5; N, 11·8%). The Os/N ratios corresponding to these analytical data are 3/7·17, 3/7·05, and 3/7·12, respectively.

In order to determine the fraction of the nitrogen liberated upon treatment with concentrated sodium hydroxide solution, a modified Kjeldahl procedure[4] was used. A 0·2529 g sample of a product containing 11·9 per cent total nitrogen was treated with 45% NaOH solution, the ammonia liberated was collected in saturated boric acid solution and titrated with 11·0 ml of 0·1032 N hydrochloric acid solution using bromcresol green indicator. From these data it was calculated that 52·8 per cent of the nitrogen present was liberated. From an entirely independent experiment a value of 56·3 per cent was found.

On the assumption that the empirical formula of the solid reaction product was $Os_3N_7O_9H_{21}$, four experiments were conducted to establish the constancy of the mole ratio of OsO_4 consumed to solid product formed; the resulting data are given in Table 1.

Thermal decomposition of solid product

Additional information concerning the composition of the solid reaction product was obtained by analysis of its decomposition products. Since this solid decomposes with explosive violence, it was decomposed in a stainless steel autoclave (3 × 13 cm) fitted with a needle valve and a thin lead gasket.

Weighed samples of the solid were placed in the autoclave which was then evacuated for 24 hr. The solid was decomposed by cautiously heating the autoclave with a Meeker burner flame for 1 hr.

[3] For further details concerning equipment see: E. M. POTRAFKE, Thesis, The University of Texas (1960).
[4] L. W. WINKLER, *Z. Angew. Chem.* **27**, 630 (1914).

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The gaseous decomposition products were removed with a Toepler pump for analysis;* the results are given in Table 2. Run No. 1 employed 0·4982 g of the solid reaction product; 61·4 cm³ of gaseous products was collected at 748 mm and 28°. In Run No. 2, 0·4972 g of solid yielded the same volume of gas collected under the same conditions. The solid residue remaining in the autoclave was removed for analysis and found to consist of 96 per cent elemental osmium. An X-ray diffraction pattern was identical with that for pure osmium and included no extraneous lines.

TABLE 1.—SOLID PRODUCT FORMED IN OSMIUM TETROXIDE–AMMONIA REACTIONS

OsO_4 (mole × 10^3)	Time, (hr)	Solid product (g)	Solid product, (mole × 10^3)	
			Calc.	Found
2·12	5	0·5764	7·07	6·91
1·47	6	0·3935	4·88	4·72
2·04	8	0·5607	6·78	6·72
1·30	17	0·3636	4·34	4·36

TABLE 2.—ANALYSIS OF GASEOUS PRODUCTS OF DECOMPOSITION OF $Os_3N_7O_9H_{21}$

Component	Mole per cent	
	Run No. 1	Run No. 2
N_2	72·2	75·0
NH_3	13·1	10·8
H_2	10·9	8·90
CH_4	2·7	3·4
H_2O	0·88	1·4
CO_2	0·07	0·41
N_2H_4	0·06	0·02
O_2	0·07	0·07

Other properties of the solid product

None of these products gave a satisfactory X-ray diffraction pattern. Only three rather diffuse lines were observed; the corresponding *d*-spacings (Å) (relative intensities in parentheses) are: 4·56 (1·0), 3·96 (0·9), 3·79 (0·5).

The magnetic susceptibility of the solid product from several independent experiments was determined; in all cases the product was found to be diamagnetic.

Although extensive studies of the infra-red spectra were not undertaken, it was demonstrated that (using KBr disks) this product exhibits rather poorly defined absorption maxima at 1020, 1073, 1300, 1370, and 3400 cm^{-1}. Attempts to obtain more satisfactory results by using Nujol mulls or by varying the concentration in KBr were unsuccessful.

Efforts to find a solvent for this product were unrewarding. It was found to be insoluble (both at room temperature and at elevated temperatures) in sixteen different solvents including water, ethanol, phenol, γ-butyrolactone, dimethylsulphoxide, dimethylformamide, and acetic and hydrochloric acids. In all of these tests the solid behaved as a single homogeneous substance.

The gaseous reaction product

Owing to the necessarily small samples of OsO_4 used and the consequently small volumes of water-insoluble gas liberated, accurate measurement of the latter required scrupulous elimination of even

* By the Mass Spectrograph Laboratory, The University of Texas.

small sources of error (e.g., leakage of air into the system, or failure to remove completely gases dissolved in the water over which the gas (N_2) was collected).

In five experiments employing from 2·04 to 9·25 mole ($\times 10^3$) of OsO_4, the resulting N_2/OsO_4 ratios averaged 0·27 ± 0·04/1. The comparable data from two experiments in which it is believed that essentially all sources of error were eliminated were (for both experiments), 0·34/1.

Establishment of the osmium tetroxide–ammonia reaction ratio

In an experiment designed to measure accurately the quantity of ammonia consumed in the reaction, ammonia was delivered from a gas burette to a reaction vessel containing OsO_4 (9·08 mole $\times 10^3$). After contact for 14 hr, the volume of ammonia consumed was measured and found to be (also in mole $\times 10^3$) 28·2; this corresponds to an NH_3/OsO_4 ratio of 3·11/1. Thereafter, the reaction mixture was allowed to stand for an additional 46 hr, whereupon the ratio was found to have increased only slightly, i.e., to 3·32/1. Finally, the pressure in the reaction vessel was reduced to ca. 10^{-3} mm for 24 hr and anhydrous ammonia gas was then re-admitted to the reaction vessel. The solid reaction product was found to adsorb only $5·2 \times 10^{-3}$ mole of ammonia; this is equivalent to 0·57 mole NH_3/mole OsO_4 used initially.

Measurement of weight of water formed

In a single experiment of this type, the reaction of OsO_4 (1·30 mole $\times 10^3$) with ammonia was allowed 17 hr for completion and the weight of the solid product in an ammonia atmosphere at room temperature was found to be 0·3868 g. The pressure was reduced to 10^{-3} mm for 24 hr, after which the weight was re-determined under conditions identical with those given above and found to be 0·3436 g. If the weight loss is interpreted as solely attributable to water, the difference in weight corresponds to 1·29 mole H_2O ($\times 10^3$) as compared with the anticipated value of 1·30.

The reaction of osmium tetroxide with liquid ammonia

Liquid ammonia (15 ml) was condensed at −70° in a reaction vessel containing 0·4 g OsO_4 in a glass ampoule. When the latter was broken, the tetroxide dissolved readily to form a deep red solution.* After 4 hr the solvent was evaporated; a water-insoluble gas (presumably N_2) was collected but not analysed, and a black residue remained in the reaction vessel. (Found: Os, 70·9; N, 11·8. Calc. for $Os_3N_7O_9H_{21}$: Os, 68·5; N, 11·8%). The X-ray diffraction pattern for this solid was identical with that for the solid product of the interaction of OsO_4 and gaseous NH_3.

DISCUSSION

That equation (1) describes the interaction of osmium tetroxide with either gaseous or liquid ammonia is amply demonstrated by the foregoing data. Only the data relative to ammonia consumed and water formed in the reaction are subject to reasonable doubt. The NH_3/OsO_4 reaction ratio of 3·32/1 is higher than that implied by equation (1). This is understandable however since water present as a reaction product and/or adsorption of ammonia by the solid reaction product could account for the apparently excessive consumption of ammonia. In fact, it was demonstrated independently that adsorption alone could account for as much as 0·57 mole of NH_3/mole of OsO_4 used in the reaction. The validity of the measurement of water formed in the reaction is even more subject to question. The excellent agreement between the anticipated and measured weight loss is based upon the assumption that this loss is wholly attributable to removal of water. It is more likely that both water and adsorbed ammonia were removed; hence the correspondence referred to above may be entirely fortuitous.

The empirical formula, $Os_3N_7O_9H_{21}$, for the solid product is only one of several that have to be considered; however, it is the only one compatible with all of the data

* For recent evidence for the existence of $OsO_4.NH_3$ see: M. L. Hair and P. L. Robinson, *J. Chem. Soc.* 1960, 2775.

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given above. Further confirmation is provided by a detailed examination of the thermal decomposition products which included only elemental osmium and gaseous products (Table 2). The appearance of CH_4 and CO_2 was certainly not expected; however it is well known that the decarbonization of steel occurs in the presence of hydrogen and oxygen at temperatures above 400°.[5] Otherwise, a number of useful computations can be made using, for example, the data for Run No. 1, Table 2. The total nitrogen accounted for by the analysis of gaseous decomposition products is 0·0574 g as compared with 0·0588 g of nitrogen in the sample of $Os_3N_7O_9H_{21}$ decomposed. Similar calculation of the total hydrogen represented by the gaseous products leads to a value that is low (0·00192 g) relative to the total hydrogen (0·0126 g) in the sample of $Os_3N_7O_9H_{21}$. If the difference is attributed to water retained in the solid residue (i.e., not removed by the Toepler pump), the corresponding weight of H_2O is 0·0963 g. Given this value we may calculate the *total* oxygen represented by all of the thermal decomposition products and compare this value with the oxygen content of the sample decomposed; these values are 0·0860 and 0·0863 g, respectively. Finally, the total hydrogen and nitrogen found by analysis of the decomposition products lead to a H/N ratio of 3·07/1 which further supports the empirical formula for the osmium-containing reaction product. Similar and equally convincing calculations can be made using the data from Run No. 2, Table 2. Unfortunately, the formula could not be further confirmed by molecular weight determinations owing to unfavorable solubility characteristics and the rather unsatisfactory X-ray diffraction patterns.

With reference to the structure suggested above, it is recognized at the outset that the present studies in no sense provide proof. Nevertheless, innumerable structures have been considered and this one (or some minor variation thereof) is the only one that is tenable in the light of all of the facts available.

First, we conclude that all of the osmium is in the 6+ oxidation state, and for the following reasons. The compound is diamagnetic, and VASKA[1] has pointed out that paramagnetism is exhibited only by compounds of $Os^{3+,4+,5+}$ and that all known compounds of $Os^{2+,6+}$ are diamagnetic.* Also, the half-reaction for the production of *one* mole of nitrogen/*three* moles of osmium tetroxide by the oxidation of ammonia is,

$$2NH_3 \rightarrow N_2 + 6e^- + 6H^+ \qquad (2)$$

or $2e^-$/Os. Furthermore, there are two 5*d* electrons in Os^{6+} and this permits the addition of sixteen electrons to result in a dodecahedral[6] d^4sp^3 hydrid. It is seen by inspection of the foregoing formula that this number of electrons about each osmium atom is implied.

Second, the non-equivalence of the nitrogen atoms has been demonstrated by the fact that 4/7 of the total nitrogen is liberated as ammonia upon treatment with sodium hydroxide. This is interpreted as corresponding to the four "co-ordinated" ammonia molecules represented in the above structure. Further support for this interpretation is found in the fact that VASKA[1] has shown that bonds between osmium and nitrogen as amide, imide, or nitride groups are not ruptured under the conditions employed in the present work.

* For a recent exception see: G. B. HARGREAVES and R. D. PEACOCK, *Proc. Chem. Soc.* 1959, 85; K. A. K. LOTIT and M. C. R. SYMONS, *J. Chem. Soc.* 1960, 973.

[5] N. P. INGLIS and W. ANDREWS, *J. Iron Steel Inst.* **128**, 383 (1933).

[6] G. E. KIMBLE, *J. Chem. Phys.* **8**, 188 (1940).

Finally, the infra-red spectral data are of interest although not conclusive The bands at 1020 and 1073 cm^{-1} are probably those previously attributed to the Os—N vibration.[7] The band at 3400 cm^{-1} may be due to O—H stretching although it is somewhat higher than ordinarily associated with this functionality. The bands at 1300 and 1370 cm^{-1} cannot be assigned on the basis of available data.[8,9]

[7] J. LEWIS and G. WILKINSON, *J. Inorg. Nucl. Chem.* **6**, 12 (1958).
[8] L. A. WOODWARD and H. L. ROBERTS, *Trans. Faraday Soc.* **52**, 615 (1956).
[9] R. E. DODD, *Trans. Faraday Soc.* **55**, 1480 (1959).

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J. Inorg. Nucl. Chem. 1960, Vol. 17, pp. 254 to 256. Pergamon Press Ltd. Printed in Northern Ireland

IODINE MONOCHLORIDE AND IODINE TRICHLORIDE COMPLEXES WITH HETEROCYCLIC AMINES

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(*Received* 16 *September* 1960; *in revised form* 26 *September* 1960)

Abstract—Molecular addition compounds of iodine monochloride with 4-picoline, quinoline, and piperidine, and of iodine trichloride with pyridine, 2-picoline, 4-picoline, 2,6-lutidine, quinoline, and piperidine have been prepared. The stoichiometry of these compounds is 1 : 1 in amine to iodine chloride. Comparisons of melting points are made and the trend interpreted as reflecting a greater degree of ionic character in iodine trichloride complexes with amines as compared with iodine monochloride complexes with similar amines.

INTEREST in molecular addition compounds of iodine monochloride and other iodine halides with various electron donor systems has arisen in the last few years. MULLIKEN's charge transfer theory[1] has satisfactorily explained the bonding in such compounds. Relatively strong electron donors like heterocyclic amines form stable, solid compounds with iodine monochloride and iodine trichloride. Some compounds of this nature have been reported in the literature.[2–5]

The present work was undertaken to investigate corresponding series of compounds of iodine monochloride and iodine trichloride for the purpose of comparing their properties. All of the compounds studied were found to consist of a 1:1 mole ratio of amine to iodine chloride.

EXPERIMENTAL†

Chemicals

Carbon tetrachloride was used as the solvent in all experiments. Matheson Co. carbon tetrachloride was dried over anhydrous calcium chloride for several days and fractionated. All amines were obtained from Eastman Kodak Co. They were dried over potassium hydroxide for several days and fractionated. Only constant boiling middle cuts of carbon tetrachloride and the amines were collected, and all boiling points were within three degrees or less of literature values.

Iodine monochloride was prepared and purified by the method of CORNOG and KARGES[6]. Iodine trichloride was prepared by the method of BOOTH and MORRIS[7].

Solutions were prepared by direct weighing. Usually, 0·1 M solutions of both reagents were employed. The iodine monochloride or iodine trichloride solution (usually 100 ml) was added from a burette to an equal volume of amine solution with constant stirring. The solid product was collected by suction filtration, washed with solvent until the washings were colourless, and placed in a desiccator. A slight excess of the iodine chloride solution was added so that the reported yields are based

* Taken in part from a thesis presented by C. W. HICKAM to Washington and Lee University in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

† Melting points are corrected.

[1] S. P. MCGLYNN, *Chem. Rev.* 1113 (1958).
[2] E. V. ZAPPI and M. FERNANDEZ, *An. Asoc. Quim. Argentina* **27**, 102 (1939).
[3] A. I. POPOV and R. T. PFLAUM, *J. Amer. Chem. Soc.* **79**, 570 (1957).
[4] A. I. POPOV and R. H. RYGG, *J. Amer. Chem. Soc.* 4622 (1957).
[5] A. I. POPOV, C. C. BISI and M. CRAFT, *J. Amer. Chem. Soc.* **80**, 6513 (1958).
[6] J. CORNOG and R. A. KARGES, *Inorganic Syntheses* Vol. 1, p. 165. McGraw-Hill, New York (1939).
[7] H. S. BOOTH and W. C. MORRIS, *Inorganic Syntheses*, Vol. 1, McGraw-Hill, New York (1939). p. 167.

on the amines. It was found in some cases that the yields could be somewhat improved by using higher concentrations of reagents. However, since 0·1 M solutions are convenient to handle, all the stated yields apply to solutions of this concentration. Varying the volume of reagents used had no effect on yield.

The compounds are sparingly to moderately soluble in cold water but decompose rapidly in boiling water with the liberation of iodine. Chlorine content was determined by boiling the sample to be analysed [0·2–0·3 g] in a little water [10–15 ml] until iodine vapours ceased to be liberated and the solution was pale yellow. The standard Volhard method was used to analyse for chloride ion.

4-*Picoline*–ICl. Yellow powder. m.p. 107–108° Yield 89%. (Found*: C, 28·32; H, 2·79; Cl, 13·94. Calc. for C_6H_7NICl: C, 28·20; H, 2·77; Cl, 13·88%).

TABLE 1.—MELTING POINTS OF MOLECULAR ADDITION COMPOUNDS OF IODINE MONOCHLORIDE AND IODINE TRICHLORIDE WITH SOME HETEROCYCLIC AMINES

Amine	m.p. ICl compd. (°C)	m.p. ICl_3 compd. (°C)
Pyridine	133[4]	175–177
2-Picoline	77·5[4]	131–133*
4-Picoline	107–108*	133–134*
2,6-Lutidine	112–113[4]	103–105*
Quinoline	150–152	134–139
Piperidine	dec. 92*	dec. 124–125*
2,2′-Bipyridine	dec. 95[3]†	
Pentamethylenetetrazole	116–118[5]	

* Previously unreported.
† The stoicheometry of this compound is not 1 : 1 but is 2 : 1 in ICl to amine.

Quinoline–ICl. Lemon-yellow powder. m.p. 150–152° [Lit.[2] 157°] Yield 100 per cent. (Found: C, 37·27; H, 2·35; Cl, 12·41. Calc. for C_9H_7NICl: C, 37·07; H, 2·42; Cl, 12·16%).

Piperidine–ICl. White powder which slowly darkens over a period of several days. The presence of moisture hastens this decomposition slightly. m.p. dec. 92° Yield 95 per cent. (Found: C, 24·45; H, 4·50; Cl, 14·39. Calc. for $C_5H_{11}NICl$: C, 24·26; H, 4·49; Cl, 14·32%).

Pyridine–ICl_3. Lemon-yellow powder. m.p. 175–177° [Lit.[2] dec. 196°] Yield 80 per cent. (Found: C, 19·36; H, 1·43; Cl, 34·57. Calc. for $C_5H_5NICl_3$: C, 19·22; H, 1·62; Cl, 34·06%).

2-*Picoline*–ICl_3. Lemon-yellow powder which becomes slightly darker yellow on standing. m.p. 131–133° Yield 56 per cent. (Found: C, 21·81; H, 2·15; Cl, 32·67. Calc. for $C_6H_7NICl_3$: C, 22·08; H, 2·17; Cl, 32·59%).

4-*Picoline*–ICl_3. Lemon-yellow powder which becomes somewhat orange on standing; slightly hygroscopic. m.p. 133–134° Yield 88 per cent. (Found: C, 22·00; H, 2·08; Cl, 32·38. Calc. for $C_6H_7NICl_3$: C, 22·08; H, 2·17; Cl, 32·59%).

2·6-*Lutidine*–ICl_3. Yellow powder; hygroscopic. m.p. 103–105° Yield 65 per cent. (Found: C, 24·55; H, 2·75; Cl, 31·38. Calc. for $C_7H_9NICl_3$: C, 24·69; H, 2·67; Cl, 31·25%).

Quinoline–ICl_3. Pale yellow powder. m.p. 134–139° [Lit.[2] 152–160°] This compound consistently melted reversibly over the stated range. Yield 83 per cent. (Found: C, 29·76; H, 1·88; Cl, 29·03. Calc. for $C_9H_7NICl_3$: C, 29·82; H, 1·95; Cl, 29·35%).

Piperidine–ICl_3. Lemon-yellow powder which becomes somewhat orange on standing. m.p. dec. 124–125°. This compound rapidly attacked a nickel spatula and liberated iodine. Yield 60 per cent. (Found: C, 19·07; H, 3·55; Cl, 33·88. Calc. for $C_5H_{11}NICl_3$. C, 18·86; H, 3·49; Cl, 33·40%).

DISCUSSION

Table 1 summarizes the melting point data for iodine monochloride and iodine trichloride addition compounds with heterocyclic amines.

* C, H analyses performed by Galbraith Laboratories, Knoxville, Tenn.

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For a 1:1 addition compound involving iodine monochloride, the molecule is thought to be stabilized by resonance between two principal contributing structures:[1]

Donor ICl
I

Donor $I^+ \ldots . Cl^-$
II

An estimate of 50 per cent ionic character for the Pyridine–ICl compound has been made.[8] Presumably, in the case of the 1:1 compounds of ICl_3, the principal contributing structures are:

Donor ICl_3
I

Donor $ICl_2^+ \ldots . Cl^-$
II

Structure II should become more important as the electron donating ability of the donor molecule increases and as the electron accepting ability of the iodine chloride molecule increases.

The addition of the electronegative chlorine atoms will tend to make ICl_3 a better electron acceptor than ICl with a given donor molecule, other factors being equal. Hence we may expect a correspondingly higher degree of ionic character in an addition compound with a given amine and ICl_3 as compared with the addition compound of the same amine with ICl. This factor may partially explain the rather striking increase in the melting points of the ICl_3 compounds of pyridine, 2-picoline, 4-picoline, and piperidine as compared with those of the ICl compounds of these amines. The slight decrease in the melting point of the 2,6-Lutidine-ICl_3 compound as compared with the 2,6-Lutidine–ICl compound is not surprising. 2,6-Lutidine may be a weaker electron donor toward ICl_3 than toward ICl because of steric hindrance. Certainly, the larger, more bulky ICl_3 molecule will be more susceptible to steric interference than the smaller ICl molecule. The melting point of the Quinoline–ICl_3 compound appears to exhibit anomalous behavior, but steric hindrance may be a factor here also.

The disagreement in the melting points of the Pyridine–ICl_3 and Quinoline-ICl_3 compounds as found in this work and as reported by ZAPPI and FERNANDEZ[2] is beyond experimental error. ZAPPI and FERNANDEZ relied solely upon iodometric equivalence in the characterization of these compounds. In view of the agreement between theoretical and experimental values for the carbon, hydrogen and chlorine contents of the compounds prepared in this study, we feel that the melting point data reported herein are accurate.

Acknowledgment—We wish to express our appreciation for a John M. Glenn Grant, which partially supported this work.

[8] W. B. PEARSON, R. E. HUMPHREY, W. A. DESKIN and A. I. POPOV, *J. Amer. Chem. Soc.* **80**, 2049 (1958).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 257 to 264. Pergamon Press Ltd. Printed in Northern Ireland

AMINE DERIVATIVES OF VANADIUM AND NIOBIUM PENTAFLUORIDES*

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(*Received* 30 *August* 1960; *in revised form* 26 *September* 1960)

Abstract—The reactions of vanadium pentafluoride with ammonia, pyridine and ethylenediamine produce amminotetrafluorovanadium (IV), pyridinetetrafluorovanadium (IV) and tris(ethylenediamine)tetrafluorovanadium (IV) respectively. Niobium pentafluoride reacts with ammonia and ethylenediamine to give diamminopentafluoroniobium (V) and a product of composition $NbF_5(en)_{1\cdot6}$. The infra-red spectra of these new compounds are discussed and the reasons for the production of these compounds are considered in terms of maximum co-ordination state and fluorine-bridge bonding.

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UNTIL recently, few detailed studies had been made of the volatile transition metal fluorides because of their extreme reactivity with traces of moisture and standard vacuum greases. Recent work has shown that with careful purification and the rigorous exclusion of moisture, these fluorides can be readily handled in glass apparatus.[1] Such techniques have been used to study some of the chemical and physical properties of vanadium, niobium and tantalum pentafluorides[2] and tungsten hexafluoride.[3] These fluorides are reported to form adducts with nitrogen bases; niobium and tantalum pentafluorides form adducts $MF_5 \cdot 2Py$ with pryidine, and tungsten hexafluoride gives the products $WF_6 \cdot 3Py$, $WF_6 \cdot (MeNH_2)_3$ and $WF_6 \cdot 4NH_3$ with pyridine, methylamine and ammonia respectively. The structures of these presumably co-ordinated derivatives are not immediately apparent, especially in the case of the tunsten hexafluoride derivatives where it seems necessary to invoke nine or ten co-ordination of tungsten. As a first step towards clarifying the situation we have studied the reactions of vanadium and niobium pentafluorides with ammonia, pyridine and ethylenediamine.

EXPERIMENTAL

Vanadium and niobium pentafluorides were prepared by passing gaseous fluorine diluted with nitrogen over the powdered metals in a nickel tube heated to 325–350°. The products were collected in dry, all-glass systems with traps cooled to −78°. Niobium pentafluoride prepared in this way was used without further purification (Found: Nb, 49·3. Calc. for NbF_5; Nb, 49·4%). It was stored in sealed traps until required and then transferred to the reaction tubes in a dry-box. The vanadium pentafluoride was re-distilled from dry sodium fluoride in an all-glass system before use (Found: V, 35·3; F, 64·1; Calc. for VF_5: V, 34·9; F, 65·1%).

All reactions were performed in all-glass vacuum systems with taps replaced by combinations of capillary constrictions and magnetic break-seals. Before use the systems were carefully "flamed out" under vacuum to ensure the complete absence of moisture. The volatile reaction products were collected in similar trap-lines. All reagents were carefully dried before reaction with the pentafluorides.

* Presented at the 137th National Meeting, American Chemical Society, Cleveland, April, 1960.

(1) T. A. O'DONNELL, *J. Chem. Soc.* 4681 (1956).
(2) H. C. CLARK and H. J. EMELÉUS, *J. Chem. Soc.* 2119 (1957); 190 (1958).
(3) H. C. CLARK and H. J. EMELÉUS, *J. Chem. Soc.* 4778 (1957).

Vanadium was estimated by reduction with sulphur dioxide followed by titration with standard 0·01 N potassium permanganate. Niobium was estimated by precipitation of the hydrated oxide from ammoniacal solution followed by ignition to the pentoxide. Ethylenediamine, which interfered in both these determinations, was first removed by oxidation with mercuric oxide–sulphuric acid. The most dependable method for the determination of fluorine was found to be precipitation as lead chlorofluoride. A preliminary separation of fluoride from interfering ions was most satisfactorily achieved by distillation from a sulphuric acid solution at 135°.[4] However, in certain cases, particularly the vanadium compounds, the fluoride analysis was not reliable despite repeated analyses, and it was then necessary to neglect this figure in establishing the constitution of the solid products. Nitrogen was estimated by the standard micro-Kjeldahl method. Carbon and hydrogen analysis were by Dr. A. Bernhardt, Mulheim, Germany. Magnetic susceptibilities were determined with a Gouy-type magnetic balance and infra-red spectra were recorded on a model 21 double beam Perkin-Elmer recording spectrophotometer. The samples were prepared in potassium bromide pellets which were then sandwiched between pure potassium bromide pellets to prevent hydrolysis of the fluoride.

Reaction of vanadium pentafluoride and ammonia

An excess of anhydrous ammonia (Matheson Co.) was distilled twice in a dry, all-glass system from sodium metal and thence onto vanadium pentafluoride. An orange-brown solid, insoluble in liquid ammonia, was formed immediately. To ensure complete reaction, the ammonia in the reaction trap was kept liquid for several hours. Excess ammonia, along with any volatile products, was distilled *in vacuo* through traps cooled to −196°, −78° and 0°, but the only volatile material was found to be ammonia. A powdery, reddish-brown solid remained, which, in sealed tubes, slowly decomposed, building up a pressure of ammonia. This solid was then pumped at room temperature for several hours leaving a light grey solid of composition $VF_5 \cdot 2NH_3$ (Found: V, 28·8; NH_3, 19·5. Calc. for $VF_5 \cdot 2NH_3$: V, 28·35; NH_3, 18·9%). The only volatile material removed during pumping was ammonia, identified spectroscopically. The product $VF_5 \cdot 2NH_3$ had a magnetic moment of 2·1 B.M. at 20°, approximating to the value for the one unpaired electron of quadrivalent vanadium. The product formed green aqueous solutions and titration of a fresh solution with standard permanganate (0·01 N) indicated that the vanadium was present principally as V(IV) with a small amount (8 per cent) of V(III). An X-ray powder photograph showed the product to contain ammonium fluoride. This was removed by heating the mixture under vacuum at 100° for 120 hr. The product finally obtained was a greyish brown powder of composition $VF_4(NH_3)$, amminotetrafluorovanadium (IV). (Found: V, 34·7; NH_3, 12·5. Calc. for $VF_4(NH_3)$: V, 35·4; NH_3, 11·8%). The slight discrepancy of the observed figures corresponds to the presence of approximately 0·08 mole of ammonium fluoride which could not readily be removed. When heated in a sealed tube, $VF_4(NH_3)$ did not melt but decomposed about 250°, etching the glass tube and forming a lustrous black solid. Amminotetrafluorovanadium (IV) was not soluble in dried organic solvents such as benzene, carbon tetrachloride, ethanol (100 per cent), ether, nitrobenzene and pyridine, and further purification of the compound was therefore not possible.

Reaction of vanadium pentafluoride and pyridine

An excess of Eastman-Kodak reagent grade pyridine was distilled in vacuum from crushed potassium hydroxide on to vanadium pentafluoride. Reaction occurred immediately at −78° forming a dark brown solid which was insoluble in pyridine. Volatile reaction products and excess pyridine were removed in vacuum and passed through traps cooled to −23°, −78° and −196°. The brown residue was pyridinetetrafluorovanadium (IV), $(C_5H_5N)VF_4$ (Found: V, 24·6; F, 35·0; C, 30·3; N, 6·2; H, 3·5. Calc. for $C_5H_5NVF_4$: V, 24·7; F, 36·9; C, 29·2; N, 6·8; H, 2·4%) which had a magnetic moment of 1·67 B.M. at 20°. Titration of a fresh aqueous solution of the compound with standard permanganate confirmed the quadrivalency of vanadium. The volatile fraction condensing at −23° was found to be pyridine; it also gave a positive qualitative test for fluoride, but it was not found possible to isolate or identify this reactive fluoride species. The only other volatile fraction, which condensed in the −78° trap, was pure pyridine.

Pyridinetetrafluorovanadium (IV) was slowly hydrolysed in air, dissolved quickly in water forming a green solution, and was insoluble in common organic solvents. When heated in a sealed tube, pyridinetetrafluorovanadium (IV) did not melt but decomposed about 150°.

[4] H. H. WILLARD and O. B. WINTER, *Industr. Engng. Chem.* Analyt. Ed. **5**, 7, (1933).

Reaction of vanadium pentafluoride and ethylenediamine

The procedure was the same as that described in the above experiments. The involatile reaction product was dark brown, tris(ethylenediamine)tetrafluorovanadium (IV), $VF_4(en)_3$. (Found: V, 16·9; F, 24·9; N, 24·1; C, 23·7; H, 7·3. Calc. for $C_6N_6H_{24}VF_4$: V, 16·7; F, 24·8; N, 27·1; C, 23·4; H, 7·9%). The magnetic moment was 2·0 B.M. confirming the quadrivalent state of vanadium, but because of interference by the ethylenediamine, the valence state of vanadium could not be checked by titration with standard permanganate. Only ethylenediamine was found in the volatile fractions which condensed at −78° and −23°. No trace of fluoride or any combined fluorine was found in these fractions.

Tris(ethylenediamine)tetrafluorovanadium (IV) was insoluble in benzene, carbon tetrachloride, ether, ethanol, nitrobenzene and pyridine. It dissolved quickly in dilute acid, but was not markedly hygroscopic and could be handled in air without noticeable decomposition. No melting point was observed since the solid decomposed at temperatures over 160°.

Reaction of niobium pentafluoride and ammonia

The product of this reaction, carried out as described above, was a brilliant yellow solid, insoluble in liquid ammonia. The solid was diamminopentafluoroniobium (V), $NbF_5 \cdot 2NH_3$. (Found: Nb, 41·9; F, 41·5; NH_3, 15·3. Calc. for $NbF_5N_2H_6$: Nb, 41·9; F, 42·8; NH_3, 15·3%). Diammino-pentafluoroniobium (V) hydrolysed slowly in moist air and dissolved quickly in water. It melted about 300–310° with some decomposition and extensive etching of the glass tube. The compound was diamagnetic confirming that only niobium (V) was present, and an X-ray powder photograph did not reveal lines due to ammonium fluoride.

The dissociation pressure of diamminopentafluoroniobium (V) was measured over the range 50–100° with an all-glass, Pyrex spiral gauge which has been previously described.[8]

Reaction of niobium pentafluoride and ethylenediamine

A slow reaction occurred at room temperature between dry ethylenediamine and niobium pentafluoride (0·50 g) to give, after several hours, a dark brown syrup from which ethylenediamine could only be removed with difficulty. The viscous brown liquid was heated to 90–95° *in vacuo* for 12 hr; this removed all but 0·257 g of ethylenediamine and transformed the liquid into a glassy, easily pulverised solid, whose composition from analysis and weight gain was $NbF_5(en)_{1\cdot6}$. (Found: Nb, 32·6; F, 33·4. Calc. for $NbF_5(en)_{1.6}$: Nb, 32·7; F, 33·4%). Only ethylenediamine was removed from the liquid during the prolonged heating. The solid product, $NbF_5(en)_{1\cdot6}$, was readily soluble in water but was not appreciably hydroscopic and could be handled in the air. Decomposition, rather than melting, occurred about 240°.

DISCUSSION

The reactions of vanadium pentafluoride with ammonia, pyridine and ethylenediamine are all characterised by the formation of quadrivalent vanadium compounds, amminotetrafluorovanadium (IV), pyridinetetrafluorovanadium (IV), and tris-(ethylenediamine)tetrafluorovanadium (IV) respectively. The quadrivalent state of vanadium was confirmed by the observed magnetic moments of 1·7–2·1 B.M. and where possible by direct titration with standard permanganate.

Niobium pentafluoride, however, is not reduced in its reactions with these bases but forms 1:2 adducts with ammonia and pyridine, while the ethylenediamine product, $NbF_5(en)_{1\cdot6}$, could reasonably be regarded as a highly solvated 1:1 adduct, $NbF_5(en)$ and thus be considered similar to the 1:2 adducts formed by the unidentate ligands.

The dissociation pressure of diamminopentafluoroniobium (V), measured over the range 50–100°, was found to obey the linear relation

$$\left[\log p_{(\mathrm{mm})} = 5{\cdot}62 - \frac{1720}{T}\,.\right]$$

This linear Clausius-Clapeyron plot suggests that the two ammonia molecules dissociate simultaneously, and the following thermodynamic values have been calculated on the assumption that the dissociation occurs as follows:

$$NbF_5(NH_3)_2(s) \rightleftharpoons NbF_5(g) + 2\,NH_3(g).$$

The thermodynamic values of the ammonia and pyridine[5] derivatives are given in Table 1.

TABLE 1.—THERMODYNAMIC CONSTANTS OF NbF_5 ADDUCTS

	$NbF_5(NH_3)_2$	$NbF_5(Py)_2$
Temp. of Calculations	85°	50°
$\Delta H_{DISS.}$ (cal/mole)	7870	22,960
$K_P \times 10^6$	8·85	28·4
ΔF (cal/mole)	11,540	9640
ΔS (e.u.)	10·3	41·2

TABLE 2.—INFRA-RED FREQUENCIES OF $VF_4(NH_3)$ AND $NbF_5(NH_3)_2$

$(NH_3)VF_4$		$(NH_3)_2NbF_5$		NH_3(gas)[8]		Assignment
3250	(*s,b*)	3300	(*s,b*)	3414	(ν_3)	assym N–H stretch
3100		3100		3336	(ν_1)	sym. N–H stretch
2850	(*sh*)	2850	(*sh*)			?
1650	(*wb*)	1650–70	(*sh*)	1627·5	(ν_4)	deg. NH_2 deform
1425	(*s*)	1420	(*s*)	931–968	(ν_2)	sym. NH_2 deform
1075	(*w*)	1055	(*w*)			
980	(*s*)	937	(*s*)			M–NH_2 rock.
		913	*double*			
		800	(*m,b*)			?

These values show the ammonia complex to be more stable than the pyridine complex, as would be expected if size of the ligand were an important factor in determining the stablity.

The infra-red absorption spectra of the vanadium and niobium complexes have been determined and tentative assignments, based on similarities of these spectra to those of like compounds, have been made. The simplicity of the spectra of the ammonia derivatives, the absorption bands of which are listed in Table 2, makes assignments relatively easy, particularly as the spectra can be compared with those of twenty-eight transition metal ammines, principally hexa- and penta-ammines.[6,7]

The absorption bands from 3300 to 3100 cm^{-1} are undoubtedly due to N–H stretching vibrations. Where resolved, the highest wavenumber is assigned to the asymmetric stretch, the lower to the symmetric N–H stretch. The 1650 cm^{-1} band, generally broad and weak in transition metal ammines is probably due to the degenerate NH_2 deformation frequency (1627·5 cm^{-1} in gaseous ammonia). The bands at 1425 cm^{-1} in $(NH_3)VF_4$ and 1420 cm^{-1} in $(NH_3)_2NbF_5$ are due to the symmetric NH_2 deformation frequency, which in gaseous ammonia is observed as a doublet at 968 and

[5] H. C. CLARK, Thesis, Cambridge University (1957).
[6] G. F. SVATOS, D. M. SWEENEY, S. MIZUSHIMA, C. CURRAN and J. V. QUAGLIANO, *J. Amer. Chem. Soc.* **79**, 3313, (1957).
[7] D. B. POWELL and N. SHEPPARD, *J. Chem. Soc.* 3108 (1956).
[8] G. HERZBERG, *Infra-red and Raman Spectra*. Van Nostrand, New York (1945).

937 cm^{-1}. A similarly large shift of this absorption to higher frequencies is observed in transition metal ammines. The very strong bands at 980 cm^{-1} in $(NH_3)\,VF_4$ and 937 and 913 cm^{-1} in $(NH_3)_2\,NbF_5$ are probably the metal–nitrogen rocking frequency, which is thought to occur between 1000 and 650 cm^{-1} although this assignment is by no means certain.[6,7]

Assignment of the absorption frequencies in VF_4 (Py) is less certain due to the much more complicated spectrum of the ligand. The correlation of frequencies is shown in Table 3 along with the shifts in frequencies accompanying co-ordination.

TABLE 3.—INFRA-RED ABSORPTION FREQUENCIES OF VF_4·Py

Pyridine		VF_4·Py		Assignment	Δcm^{-1}
3083		3080	(*s*)	C–H stretch	−3
		2830	(*sh*)		
		2360	(*m*)	?	
		2175	(*m*)		
		1700	(*w*)		
		1687	(*w*)		
1597		—		satellite vanishes in complexes(9)	
1583	(*s*)	1628	(*s*)		+45
1572		1543	(*s*)	C–C stretch	−29
1483		1492	(*s*)	and	+9
		1483	(*sh*)	C–N stretch	
1439		1443	(*m*)		+4
1375		1400	(*m*)		+25
		1340	(*w*)		−35
1218		1280	(*m*)		+62
1148		1255	(*m*)	Ring breathing	+107
1068		1210	(*m*)	and	+142
1130		1172	(*m*)	C–H deform	+42
		1110	(*w*)		
		1070	(*w*)		
992	(*m*)	1060	(*m*)		+68
942	(*w*)	980	(*vs*)	V–N Rocking ?	
886		835	(*w*)		−51
		785	(*sh*)		
749		758	(*s*)		+9
700		720	(*sh*)		+20
652		685	(*s*)		+33

The appearance of a very strong band at 980 cm^{-1}, where pyridine has only a weak fundamental (942 cm^{-1}), in the same frequency range as that assigned to the V–N rocking frequency in $(NH_3)\,VF_4$, suggests that this 980 cm^{-1} band may be given the same assignment. The remaining assignments are straight-forward; peaks of similar intensity in pyridine and (Py)VF_4 were matched, the sequence being chosen to give shifts to higher wavenumber of a similar order to that reported for BF_3·Py.[9] The ease with which this correlation could be made emphasizes the similarities between the spectrum of VF_4·Py and that of BF_3·Py. The source of the five weak bands between 2830 and 1687 is not known and no absorption is found in this region for BF_3·Py.

The spectral bands of the ethylenediamine complexes, as listed in Table 4, show

[9] N. N. GREENWOOD and K. WADE, *J. Chem. Soc.* 1130 (1960).

many similarities to those of other transition metal–ethylenediamine complexes.[10] As a complete assignment of these latter spectra has not yet been published, it is not possible to assign the spectra of $VF_4(en)_3$ and $NbF_5(en)_{1\cdot6}$. In addition the spectrum of the niobium derivative is probably complicated by the presence of excess ethylenediamine. Strong absorption bands occur at 915 cm^{-1} in the niobium compound and at 925–955 in the vanadium derivative. These are therefore again considered to be metal–nitrogen frequencies although the presence of an ethylenediamine absorption in that same region makes this assignment somewhat more doubtful.

TABLE 4.—INFRA-RED ABSORPTION FREQUENCIES OF ETHYLENEDIAMINE COMPLEXES

Ethylenediamine		$NbF_5(en)_{1\cdot6}$		$VF_4(en)_3$	
3350	(*s*)	3300 to 3100	*broad*	3200	(*s*)
3300	(*s*)			3110	(*s*)
2900	(*s*)			2940	(*s*)
2850	(*s*)			2340	(*m*)
		2050	(*br.sh*)	2140	(*w*)
		1600	(*s*)	1595	(*m*)
1575	(*s*)	1520	(*s*)		
1455	(*m*)	1455	(*m*)	1463	(*m*)
1350	(*m*)	1375	(*sh*)		
1310	(*m*)	1340	(*m*)	1330	(*m*)
		1275	(*s*)	1285	(*m*)
1095	(*w*)	1195	(*sh*)		
		1140	(*m*)	1130	(*w*)
1050	(*w*)	1060	(*s*)	1050	(*m*)
		1000	(*m*)	955	(*s.br*)
		915	(*br.s*)	925	
895	(*br*)				
825	(*br*)	835	(*w*)	825	(*vw*)
		750	(*br.w*)	720	(*w*)

The nature of amminotetrafluorovanadium (IV) and pyridinetetrafluorovanadium (IV) is not immediately clear. Their apparent penta-co-ordination does not seem likely and in fact little evidence is available to substantiate reports of penta-co-ordination in solids.[11] In addition, these 1:1 adducts are intractible, insoluble, non-melting solids, properties that are generally associated with polymeric structures. MUETTERTIES[12], in a study of donor complexes of the Group IV tetrafluorides, has interpreted such properties as indicative of polymerization which he has suggested may occur through the formation of fluorine bridge bonds. In view of the association via fluorine bridge bonds that has been suggested for vanadium pentafluoride,[13] it seems reasonable to suggest that $(NH_3)VF_4$ and $Py{\cdot}VF_4$ are also fluorine-bridged polymers. Through such association, the vanadium atoms in both the parent VF_5 and in the $VF_4{\cdot}$ base complexes would achieve their maximum co-ordination number of six. The maximum covalency of vanadium could also be achieved through the formation

[10] D. B. POWELL and N. SHEPPARD, *J. Chem. Soc.* 791 (1959).
[11] R. J. GILLESPIE and R. S. NYHOLM, *Quart. Rev.* 339 (1957).
[12] E. L. MUETTERTIES, *J. Amer. Chem. Soc.* **82**, 1082, (1960).
[13] See Ref. 2, also H. C. CLARK, *Chem. Rev.* **58**, 869, (1958).

of vanadium–nitrogen–vanadium polymers, but while such a structure is easily visualized for the ammonia complex, it is not easy to see how pyridine could form polymeric links of this type.

The product formed with ethylenediamine must rather be considered a complex containing the $V(en)_3^{4+}$ cation, again producing hexaco-ordination of vanadium. This would then be the first reported hexa-co-ordinate complex of quadrivalent vanadium, with the occurrence of the tetrapositive complex ion probably due to the stabilising effect of the high charge density of fluoride ions. The reduction of vanadium pentafluoride by ethylenediamine to give a derivative of the more ionic vanadium tetrafluoride is very similar to the corresponding reduction of vanadium tetrachloride by anhydrous ethylenediamine to form the ionic complex $V(en)_3Cl_3$.[14]

The derivatives of niobium pentafluoride all appear to be solvated complexes in which niobium has a minimum co-ordination number of seven. Niobium, because of its larger size, is known to show co-ordination states higher than six, the maximum for vanadium; indeed it would be possible for these derivatives of niobium pentafluoride to contain fluoride bridge bonds producing about each niobium atom a co-ordination state of eight. This difference in maximum co-ordination may well account for the different behaviour of the two pentafluorides with nitrogen bases.

It is interesting also to compare the behaviour towards nitrogen bases of the transition metal chlorides and fluorides. The highest chlorides of vanadium, niobium, tantalum, and tungsten react with ammonia, primary and secondary amines to yield solvolysed derivatives of the metal chloride[14–19]

e.g. $$VCl_4 + MeNH_2 \rightarrow VCl_3(NHMe) + HCl.$$

No reduction of the metal occurs in any of these reactions, but solvolysis occurs extensively, apparently through the base-catalysed elimination of hydrogen chloride. However, when trimethylamine was reacted with vanadium tetrachloride, reduction to tervalent vanadium occurred and a solvated complex of vanadium trichloride was isolated. Similarly, reaction[20] of molybdenum pentachloride and pyridine produced $MoCl_4 \cdot 3Py$, a derivative of quadrivalent molybdenum. In both these cases, where the elimination of hydrogen chloride cannot occur due to the lack of replaceable hydrogen, reduction of the metal takes place and the fate of the removed chlorine was never determined. These two reactions are therefore very similar to those of vanadium and niobium pentafluorides with amines. Here, also, solvolysis does not occur, suggesting that elimination of hydrogen fluoride is not energetically favoured, perhaps as a consequence of the extra stability produced by fluorine bridge bonds. The reactions of the pentafluorides with amines would then proceed through initial co-ordination of the nitrogen to the metal atom to form a donor-acceptor molecule. This will be stable and isolated as such, if the maximum co-ordination number of the central metal atom has not been exceeded. If on the other hand the maximum co-ordination number has been exceeded in this initial co-ordination step, as it would be in associated

[14] G. W. A. Fowles and W. R. McGregor, *J. Chem. Soc.* 137 (1958).
[15] G. W. A. Fowles and C. M. Pleass, *J. Chem. Soc.* 1674 ,2078 (1957).
[16] G. W. A. Fowles and F. H. Pollard, *J. Chem. Soc.* 4938 (1952).
[17] G. W. A. Fowles and D. Nicholls, *J. Chem. Soc.* 1687 (1958).
[18] G. W. A. Fowles and B. P. Osborne, *J. Chem. Soc.* 2275 (1959).
[19] G. W. A. Fowles and P. J. H. Cartmell, *J. Chem. Soc.* 4113 (1959).
[20] W. Wardlaw and H. W. Webb, *J. Chem. Soc.* 2100 (1930).

vanadium pentafluoride, then lowering of the co-ordination number is required for stabililization of the complex. If solvolysis and the elimination of hydrogen fluoride is not energetically preferable, then stability is achieved by the loss of fluorine and the reduction of vanadium. In the reaction of vanadium pentafluoride and ammonia, the remaining fluorine appears as ammonium fluoride; in the reaction with pyridine a reactive fluoride species was found to be present but was not identified; and in the reaction with ethylenediamine no information was obtained which would indicate the fate of the lost fluorine. To establish unambiguously the course of these reactions would require the identification of both the fluoride and oxidized species. In view of the intractable nature of the reaction products and their insolubility in all solvents, together with the limitations in the experimental techniques which the reactive natures of these fluorides impose, it is difficult to devise further fruitful experiments.

Acknowledgement—We gratefully acknowledge the award of a Studentship to R. G. C. from the National Research Council, Ottawa. This work was supported by the Office of Naval Research.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 265 to 272. Pergamon Press Ltd. Printed in Northern Ireland

THE DISSOCIATION OF NITRIC OXIDE–COPPER(II) HALIDE COMPLEXES IN ALCOHOLS. THE PREPARATION OF THE COPPER(II) FLUORIDE NITROSYL

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(*Received* 20 *October* 1960)

Abstract—The stability of the complexes formed between nitric oxide and cupric chloride and bromide in a series of alcohols has been studied. When cupric chloride is used, there is an equilibrium $NO + CuCl_2 \rightleftarrows CuCl_2 \cdot NO$ which tends to completion as the molecular weight of the alcohol increases. For the bromide, the reaction $NO + CuBr_2 \rightarrow CuBr_2 \cdot NO$ is complete even in methanol. After formation, both nitrosyls dissociate into ions: $CuX_2 \cdot NO \rightleftarrows CuX_3^- + NO^+$. The equilibrium constants for the dissociation of the two nitrosyls decrease in the solvents methanol to l-butanol, then begin to increase again in l-pentanol. Experiments based on these observations have made it possible to prepare for the first time the cupric fluoride nitrosyl.

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IT has been known for some time that nitric oxide and cupric bromide or chloride combine in non-aqueous solvents to form nitrosyl complexes,[1] but the composition of these complexes ($CuBr_2 \cdot NO$ and $CuCl_2 \cdot NO$, both possibly solvated) has only recently been confirmed.[2] With cupric bromide, absorption of one equivalent of nitric oxide is complete at temperatures from 0°C to at least 39°C, and at pressures differing by over 400 mm Hg. With cupric chloride this is not so, and unsuccessful attempt has been made to relate the variation in nitric oxide uptake with pressure.[3] While there is very probably a variation of nitric oxide absorbed with varying pressure, it has been found[2] that traces of water present in the solvent (particularly in alcohol) will depress the gas absorption to a far greater extent. Furthermore, evidence obtained from spectroscopic and ion-migration measurements suggests that an equilibrium

$$CuX_2 \cdot NO \rightleftarrows NO^+ + CuX_2^-$$

exists. In the visible region of the spectrum the covalent $CuX_2 \cdot NO$ is the only absorbing species, thus the optical density was used as a measure of the concentration of this species in any given solvent. This paper presents the results of experiments carried out to establish the relative stabilities of $CuBr_2 \cdot NO$ and $CuCl_2 \cdot NO$ in a series of anhydrous alcohols. The existence of the equilibrium

$$CuCl_2 + NO \rightleftarrows CuCl_2 \cdot NO$$

has been established and the values of the equilibrium constants for this reaction and $CuX_2 \cdot NO \rightleftarrows CuX_2^- + NO^+$ determined. MANCHOT[4] made the first attempt to obtain the fluoride nitrosyl, and he concluded that the bromide and chloride were the only copper(II) compounds forming nitric oxide complexes.

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EXPERIMENTAL

Reagents. Cupric bromide was prepared from cupric oxide and hydrobromic acid.[12] The compound was stored in a desiccator over sulphuric acid until required. The anhydrous cupric chloride used was reagent grade (Fisher Certified). All alcohols were refluxed with silver oxide to remove aldehydes, distilled and then refluxed with magnesium turnings and a trace of iodine to remove water. The dry alcohols were distilled off the magnesium immediately before use.

The gas handling apparatus has been described before:[13] the only modifications were the use of bottled nitric oxide (The Matheson Co., Inc.) and replacement of the gas burette by one of 10 ml capacity.

The optical measurements. A new optical cell was constructed: this was made in one piece from a length of square borosilicate glass, and had a path length of 1·001 cm. The cell was fitted with a

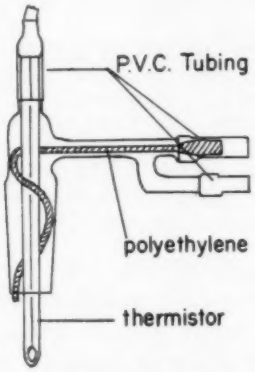

FIG. 1.—Stopper for optical cell.

standard taper socket, so that various bubbling heads could be used. Nitrosyls were prepared directly in the cell, except in the case of the copper(II) chloride compounds, which were prepared on the gas line, and then forced from the absorption bulb into the cell under an atmosphere of nitric oxide.

The optical spectra of the nitrosyls were determined on a Beckman DK2 Recording Spectrophotometer. The temperature of the nitrosyl solution was measured by a thermistor (Yellow Springs Instrument Co., Inc. 404 or 403 Probe) fitted into the cell stopper as shown in Fig. 1. This was the most satisfactory method of determining the solution temperature, although measurement with a 0·1° thermometer just before and just after the spectral determinations gave identical results.

Calculation of results. The molecular extinction coefficients of the nitrosyls were determined by optical measurements on solutions containing the copper salt, nitric oxide, alcohol and 95 per cent or more carbon tetrachloride. It was found that the dissociation of the blue complex was completely repressed at the low dielectric constants of these solutions.

(1) In cupric bromide solutions, absorption of nitric oxide is completely at one equivalent:

$$CuBr_2 + NO \rightarrow CuBr_2{\cdot}NO.$$

The blue nitrosyl formed may dissociate

$$\underset{(1-\alpha)c}{CuBr_2{\cdot}NO} \overset{Kc}{\rightleftharpoons} \underset{\alpha c}{CuBr_2^-} + NO^+,$$

and evidence for the reversibility of this reaction has been presented.[12] Further reaction may occur with the solvent:

$$\underset{(\alpha-\beta)c}{NO^+} + \underset{s}{ROH} \overset{K_1}{\rightleftharpoons} \underset{\beta c}{RONO} + \underset{\beta c}{H^+}$$

The dissociation constant Kc is given by the expression

$$\frac{[CuBr_3^-][NO^+]}{[CuBr_2 \cdot NO]} \text{ or } \frac{[CuBr_3^-][H^+][RONO]}{K_1[CuBr_2 \cdot NO][ROH]}$$

$$= \frac{(\alpha x)(\alpha - \beta)c}{(1 - \alpha)c} \text{ or } \frac{\alpha c \cdot \beta c \cdot \beta c}{K_1(1 - \alpha)c \cdot s}$$

if $\alpha \gg \beta$, $Kc \cong \frac{\alpha^2 c}{(1 - \alpha)}$

if $\alpha = \beta$ $Kc = \frac{\alpha^3 c^2}{K_1(1 - \alpha)}$.

It has been found experimentally that $\frac{\alpha^2 c}{(1 - \alpha)}$ and not $\frac{\alpha^3 c^2}{(1 - \alpha)}$ is constant (Table 2): accordingly this value is used as a measure of the stability of the nitrosyl complexes. The concentration of the undissociated nitrosyl was determined from the optical density of the solutions, the concentration of the dichloro copper(I) ion was obtained by subtraction from the volume of nitric oxide (in equivalents) absorbed by the copper salt in solution.

TABLE 1.—MOLECULAR EXTINCTION COEFFICIENTS

Compound	Solvent	Max. (mμ)	Slit (mm)	$\epsilon l_{1\,cm}$
$CuBr_2$	methanol	570	0·15	1002
	ethanol	570	0·15	1035
	l-propanol	570	0·15	1250
	l-butanol	565	0·15	614
	t-butanol	530	0·25	620
$CuCl_2$	methanol	550	0·18	1200
	ethanol	550	0·18	1000
	l-propanol	550	0·18	726
	l-butanol	560	0·16	309
	l-pentanol	548	0·18	452
	t-butanol	508	0·26	615

(2) With cupric chloride there is in addition the equilibrium $CuCl_2 + NO \rightleftarrows CuCl_2 \cdot NO$: the total combined nitric oxide is less than one equivalent ($= xc$, where $x < 1$). [NO] is taken as the volume of nitric oxide dissolved in the solvent in the absence of copper compound.

Kc is then given by the expression

$$\frac{x^2\alpha^2c^2}{x(1 - \alpha)c} = \frac{x\alpha^2c}{(1 - \alpha)}$$

and the constant for the formation of the nitrosyl is equal to

$$\frac{x(1 - \alpha)c}{[NO](1 - x)c} = \frac{x(1 - \alpha)}{[NO](1 - x)}$$

RESULTS

Values for the molecular extinction coefficients of the nitrosyl complexes are listed in Table 1. These values did not change as more carbon tetrachloride was added to the copper solutions.

Using these values, the dissociation constants for the solutions containing only the cupric halide, alcohol and nitric oxide were determined. It is seen that $\alpha^2c/(1 - \alpha)$

TABLE 2.—CONSTANCY OF K_c VALUES ($CuBr_2$ IN METHANOL)

c	$(1 - \alpha)c$	αc	$\frac{\alpha^2 c}{1 - \alpha}$	$\frac{\alpha^3 c^2}{1 - \alpha}$
$1{\cdot}25 \times 10^{-3}$M	$0{\cdot}110 \times 10^{-3}$M	$1{\cdot}14 \times 10^{-3}$M	$1{\cdot}03 \times 10^{-2}$	$1{\cdot}34 \times 10^{-5}$
2·50	0·274	2·23	1·82	4·05
3·75	0·537	3·21	1·91	6·15
4·90	0·853	4·05	1·94	7·78
6·25	1·980	4·27	1·86	39·4

TABLE 3.—VALUES OF K_c FOR $CuBr_2$ IN ALCOHOLS

Solvent	$[CuBr_2]$ M $\times 10^3$	Temperature (°C)	K_c	Average K_c
Methanol	1·25	20·4	$8{\cdot}8 \times 10^{-3}$	
	2·50		9·6	
	3·60		10·0	
	4·65		10·5	$9{\cdot}7 \times 10^{-3}$
	2·50	26·8	$1{\cdot}82 \times 10^{-2}$	
	3·75		1·91	
	4·90		1·94	
	6·25		1·86	$1{\cdot}88 \times 10^{-2}$
Ethanol	0·908	20·4	$2{\cdot}54 \times 10^{-2}$	
	1·362		2·87	
	1·817		2·75	
	2·270		2·20	$2{\cdot}5 \times 10^{-3}$
	1·20	18·2	$1{\cdot}66 \times 10^{-3}$	
	1·875		1·74	
	2·45		1·30	$1{\cdot}6 \times 10^{-3}$
1-Propanol	0·762	17·2	$1{\cdot}48 \times 10^{-4}$	
	0·896		1·50	$1{\cdot}5 \times 10^{-4}$
	0·381	22·4	$5{\cdot}0 \times 10^{-4}$	
	0·762		$5{\cdot}0 \times 10^{-4}$	$5{\cdot}0 \times 10^{-4}$
	0·762	24·0	$8{\cdot}3 \times 10^{-4}$	
	1·905		$7{\cdot}6 \times 10^{-4}$	$8{\cdot}0 \times 10^{-4}$
1-Butanol	2·050	35·5	$3{\cdot}1 \times 10^{-4}$	
	1·370		3·2	
	0·685		3·2	$3{\cdot}2 \times 10^{-4}$
	0·685	23·8°	$2{\cdot}00 \times 10^{-4}$	
	1·095		1·84	
	1·920		2·10	$2{\cdot}0 \times 10^{-4}$
	0·318	24·0	$2{\cdot}25 \times 10^{-4}$	
	0·826		2·30	
	1·321		2·02	$2{\cdot}2 \times 10^{-4}$
t-Butanol	0·981	25·0	$4{\cdot}8 \times 10^{-4}$	

and not $\alpha^3c^2/(1 - \alpha)$ is constant: the example given (Table 2) is for methanolic solutions of cupric bromide, but the same result was obtained with all the other alcohols. Values of $\alpha^3c^2/1 - \alpha)$ are not tabulated.

Values of K_c for the bromide and chloride and K_{form} for the chloride are listed in Tables 3 and 4. The only difficulties encountered in the measurements were with cupric bromide in tertiary butanol and 1-pentanol because of the very low solubility, and

with cupric chloride in methanol because of the small (0·36 equivalents) volume of nitric oxide absorbed. The methanolic solutions are by far the most sensitive to traces of water vapour. These experimental values for K_c were used to calculate $(K_c)_{20}$, the value of the dissociation constant at 20·0°C (Table 5).

TABLE 4.—VALUES OF K_{form} AND K_c FOR $CuCl_2$·NO IN ALCOHOLS

Solvent	Temperature (°C)	V_{NO} equiv.	$[CuCl_2]$ 10^3 M	$[CuCl_2$·NO$]$ 10^3 M	$[CuCl_2^-]$ 10^3 M	$[NO]$ 10^3 M	K_{form}	K_c
Methanol	29·6	0·356	7·695	1·455	2·80	1·83	$1·06 \times 10$	$5·4 \times 10^{-2}$
	20·0	0·371	7·601	0·871	3·61	1·98	5·8	$1·55 \times 10^{-2}$
Ethanol	22·2	0·824	1·205	2·05	3.59	1·44	$1·18 \times 10^2$	$6·2 \times 10^{-3}$
		0·890	0·377	0·74	1·98	1·44	1·37	6·0
	26·2	0·848	1·04	1·42	4·39	1·30	$1·05 \times 10^2$	$1·35 \times 10^{-2}$
		0·897	0·371	0·53	2·69	1·30	1·10	1·4
l-Propanol	23·4	0·792	0·232	0·578	0·305	1·08	$2·3 \times 10^2$	$2·2 \times 10^{-5}$
		0·748	0·841	2·271	0·213	1·08	2·5	2·0
	31·0	0·751	0·277	0·360	0·560	0·96	$1·35 \times 10^2$	$8·7 \times 10^{-5}$
		0·592	1·231	1·421	0·346	0·96	1·20	8·4
l-Butanol	23·4	0·698	0·64	1·24	0·18	1·04	$1·9 \times 10^2$	$2·3 \times 10^{-5}$
		0·803	0·82	2·58	0·72	1·04	2·8	2·0
	40·0	0·767	0·96	1·75	1·41	0·89	$2·1 \times 10^2$	$1·14 \times 10^{-3}$
		0·790	0·435	0·709	0·916	0·89	2·3	1·18
l-Pentanol	22·0	1·0	—	0·661	0·639	—	—	$6·2 \times 10^{-4}$
		1·0	—	0·126	0·284	—	—	6·3
	29·2	1·0	—	0·250	1·050	—	—	$4·4 \times 10^{-3}$
		1·0	—	0·148	0·825	—	—	4·6
t-Butanol	23·5	1·0	—	1·78	1·97	—	—	$2·2 \times 10^{-3}$
		1·0	—	3·05	2·66	—	—	2·3
	32·0	1·01	—	1·09	2·66	—	—	$6·5 \times 10^{-3}$
		1·0	—	1·47	3·02	—	—	6·2

TABLE 5.—$(K_c)_{20}$ VALUES

Solvent	$CuBr_2$·NO	$CuCl_2$·NO
Methanol	$9·5 \times 10^{-3}$	$1·55 \times 10^{-2}$
Ethanol	$2·3 \times 10^{-3}$	$4·1 \times 10^{-3}$
l-Propanol	$2·2 \times 10^{-4}$	$1·17 \times 10^{-5}$
l-Butanol	$1·8 \times 10^{-4}$	$1·0 \times 10^{-5}$
l-Pentanol	—	$3·8 \times 10^{-4}$
t-Butanol	$3·8 \times 10^{-4}$	$1·39 \times 10^{-2}$

DISCUSSION

Further improvements in the construction of the cell and the handling of water-free alcoholic solutions have led to higher extinction coefficients for the nitrosyls than have previously been recorded.[2,3] It is most important to prepare the alcohol immediately before use: for example, when solutions of cupric bromide were prepared in methanol distilled the day before, the molecular extinction coefficient found was 660: $\alpha^2 c/(1 - \alpha)$ was constant and ΔE was evaluated as 11 kcal/mole. When freshly dried and distilled methanol was used to prepare the solutions, values were 1002 and 19 kcal/mole respectively. The molecular extinction coefficient and dissociation constant are smallest for the 1-butanol complex in both the chloride and bromide series.

To determine whether the variation in dissociation constants of the nitrosyls was due solely to the change in dielectric constant of the solvent, a plot of $-\log (K_c)_{20}$ against the inverse of the dielectric constant was made (Fig. 2). The Born equation

predicts that such a plot should yield a straight line if the radii of the ions formed do not change in different solvents, and if the dielectric constant is not too small. Even if the dielectric constant of some of the alcohols makes a quantitative application of the Born equation impossible, we would expect a consistent trend in the values of K_c. Such is not the case: both series of nitrosyls dissociate least in 1-butanol. (the values of K_c tend methanol > ethanol > 1-propanol > 1-butanol < 1-pentanol < t-butanol. A branched chain solvent such as isopropanol (and t-butanol) forms a very unstable complex: more than would be predicted on the basis of dielectric constant alone. As it is probable that the nitrosyl complexes are solvated in alcohols, both

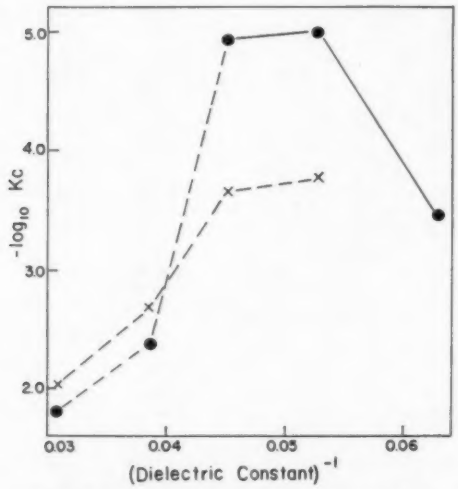

FIG. 2.—Variation of the dissociation constant with dielectric constant of the alcohols. The $(K_c)_{20}$ values for both cupric bromide nitrosyls (×) and cupric chloride nitrosyls (●) are shown

the size and the dielectric constant of the alcohol will affect the stability of the complex. The increased stability of the nitrosyls formed in 1-propanol and 1-butanol suggest that the optimum size of the solvating molecule lies between these two.

Table 4 lists the values for K_{form} for the reaction $CuCl_2 + NO \rightleftarrows CuCl_2 \cdot NO$ in methanol up to 1-butanol. It is seen from the values obtained, that the incomplete absorption of nitric oxide can be satisfactorily accounted for by such an equilibrium. When cupric bromide is the absorbing species, absorption of nitric oxide is complete in all alcohols: with cupric chloride, 1-pentanol and t-butanol are the only solvents in which this takes place.

The preparation of the copper(II) *fluoride nitrosyl.* Since both the copper(II) chloride and copper(II) bromide nitrosyls dissociate to the least extent in 1-butanol, this was the first alcohol to be tried in the preparation of the analogous fluoride compound. When nitric oxide was bubbled through a solution of cupric fluoride in 1-butanol, a violet colour appeared. The complex was unstable and disappeared in several minutes, simultaneously a white precipitate which contained both copper and fluoride formed in the solution. Conversely, although the solubility of cupric fluoride in anhydrous t-butanol is low, the nitrosyl which formed was quite stable.

The instability of the fluoride nitrosyl, which is formed only in the butanols, is

presumably due to the instability of an ion such as CuF_2^- produced in the ionization $CuF_2 \cdot NO \rightleftarrows NO^+ + CuF_2^-$ or $CuF_2 \cdot NO + ROH \rightleftarrows H^+ + RONO + CuF_2^-$. When HF was added to the 1-butanol solution, no precipitate formed, and the nitrosyl colour did not fade. It has been possible to form the cupric fluoride nitrosyl in

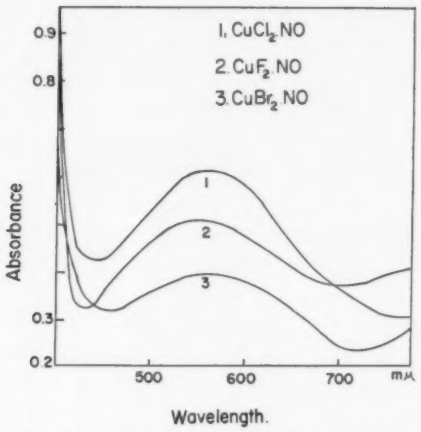

FIG. 3.—Optical spectra of the three cupric nitrosyls in 1-butanol.

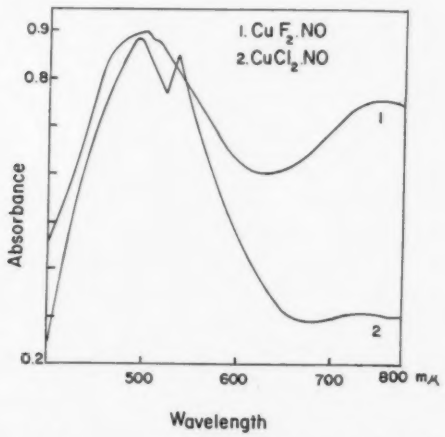

FIG. 4.—Optical spectra of cupric nitrosyls in anhydrous formic acid.

ethanol and 1-propanol in the presence of hydrogen fluoride: the complex is not formed in methanol, however: only a transient yellow colour is observed. Sodium fluoride does not appear to stabilize the nitrosyl as does the acid. Fig. 3 shows the close resemblence of the optical spectra of the three nitrosyls in 1-butanol, and a similar resemblence holds in the other solvents.

Previous work[2] has shown that concentrated sulphuric or anhydrous formic acids are the best solvents in which to form nitrosyls: the resulting solutions may be exposed to the air for several hours before the nitrosyl colour disappears completely, in contrast to the seconds required when the solvents are alcohols. Cupric formate in anhydrous formic acid does not form a complex with nitric oxide. Fig. 4 shows the

spectrum of the fluoride nitrosyl compared to that of the chloride nitrosyl previously recorded.[2]

Four different concentrations of cupric fluoride in formic acid were prepared, ranging from 0·0025 to 0·00117 M: in all four cases the absorption of nitric oxide was greater than 0·94 equivalents, and the highest reached 0·98. A solution containing 0·0054 cupric fluoride and 0·0054 cupric formate absorbed only 0·46 equivalents of nitric oxide, thus the solutions appear to behave as the cupric chloride-ethanol solutions,[2] and it appears most likely that the composition of the fluoride nitrosyl is $CuF_2 \cdot NO$, analogous to $CuCl_2 \cdot NO$ and $CuBr_2 \cdot NO$. The nitrosyl formed in formic acid is quite stable: a solution was exposed to air; after two hours the nitrosyl colour still persisted below a depth of 2·5 cm from the surface of the formic acid.

Acknowledgement—This work was supported by funds from a grant made to the Department of Chemistry, University of Ottawa by the National Research Council of Canada.

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J. Inorg. Nucl. Chem., 1961, Vol. 273, pp. 280 to 286. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF THORIUM(IV), URANIUM(IV), AND THE RARE-EARTH METAL(III) OXALATE HYDRATES. DIFFERENTIAL THERMAL ANALYSIS AND WEIGHT-LOSS STUDIES

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(*Received* 4 *August* 1960)

Abstract—Differential thermal analysis (DTA) curves are presented for thorium, scandium, uranium (IV) and the rare-earth metal oxalate hydrates. For all of the metal oxalate hydrates, endothermic and exothermic peaks are present in the curves which are the result of dehydration, decomposition, and oxidation reactions. The DTA curves for thorium and lanthanum oxalates differ from those previously reported. A weight-loss curve is presented for the thermal decomposition of the 6- and 2-hydrates of uranium (IV) oxalate.

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ALTHOUGH the chemical and physical properties of the rare-earth compounds has been investigated extensively during the past few years, the thermal stability of many of the rare-earth compounds remains perhaps the least known physical parameter. Even the ignition temperatures of the rare-earth oxalates to the metal oxides, a well known analytical procedure, remained in question until recent years when the methods of thermogravimetric analysis (TGA) precisely defined the temperature limits.

The thermal stability of the rare-earth and other metal oxalates have previously been studied by TGA and other methods. These studies include the oxalates of thorium,[1,2] scandium,[3–5] yttrium,[3–5] uranium(VI),[2] and the rare-earth elements.[3–11]

In an effort to obtain more detailed information concerning the dehydration and decomposition of these metal oxalate hydrates, the compounds were investigated by the method of differential thermal analysis (DTA). The only previous DTA study on several of these compounds was made by PADMANABHAN *et. al.*[2] who investigated the thermal decomposition of the oxalates of uranium(VI), thorium, and lanthanum. Because the above investigation was incomplete, as far as other rare-earths are concerned, this work is presented as an extension of earlier work and is concerned with all of the rare-earth oxalate hydrates, with the exception of promethium. Several discrepancies were noted in the decomposition (DTA) of thorium oxalate so it is also included as well as the oxalate of uranium(IV).

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EXPERIMENTAL

A. *Apparatus*

The automatic recording thermobalance consisted of chainomatic analytical balance to which was attached a Fisher Recording Balance Attachment. A Moseley, Model 5S, X-Y recorder was used to record the balance attachment output. The weight was recorded on the vertical axis while the temperature, as detected by a chromel–alumel thermocouple located in the furnace, was recorded on the horizontal axis. The furnace and temperature controller have previously been described.[12] Sample sizes ranged in weight from 75 to 85 mg with a furnace heating rate of 10°C per min. Samples were run in duplicate with a resultant agreement between runs of about 2 per cent on the temperature axis and 1 per cent on the weight axis.

The DTA apparatus has previously been described by LODDING and HAMMELL[13,14]. The sample and reference chambers consisted of ceramic cylinders, 0·25 in. in diameter and 0·75 in. in length. Chromel–alumel thermocouples were used to detect the differential temperatures. Output from the thermocouples was amplified by a Beckman, Model 14, breaker-type d.c. amplifier and recorded on the vertical axis of a Moseley, Model 5S, X-Y recorder. The differential temperature was plotted as a function of the temperature of the inert reference chamber. Sample size was about 100 mg, with previously ignited α-alumina being used in the reference chamber. The samples were finely powdered and loosely packed in the sample holder by gentle tamping with a glass rod. Since the amount of sample was small compared to the volume of the sample holder, the remainder of the cylinder was filled with α-alumina. The furnace heating rate was linear with time at about 10° per min.

B. *Chemicals*

The rare-earth compounds of 99·9 per cent purity were obtained as chlorides or oxides from Research Chemicals, Inc., Burbank, Calif., and the Lindsay Chemical Co., West Chicago, Ill. Scandium oxide of 99·8 per cent purity was obtained from A. D. Mackay, Inc., New York, N.Y. Uranyl nitrate 6-hydrate, reagent grade quality, was obtained from the Mallinckrodt Chemical Works, St. Louis, Mo. Thorium nitrate 4-hydrate, of high purity, was obtained from the Lindsay Chemical Co., West Chicago, Ill.

The methyl oxalate (m.p. 53°C) was prepared as previously described.[15]

All other chemicals used were of C.p. quality.

C. *Preparation of metal oxalates*

Thorium, scandium and rare-earth oxalate hydrates were prepared by the method of homogeneous precipitation with methyl oxalate as previously described.[4] All of the oxalates were analysed by ignition to the metal oxides in a muffle furnace at 900°C. The metal oxide contents agreed to within 0·5 per cent of that required by theory for the respective metal oxalate hydrates.

The uranium (IV) oxalate hydrates were prepared by the method of MARCHI[16]. The compounds were analysed by ignition to the metal oxide at 900°C. All of the metal oxide contents were within 0·2 per cent of that required by theory for $U(C_2O_4)_2 \cdot 6H_2O$ and $U(C_2O_4)_2 \cdot 2H_2O$.

RESULTS AND DISCUSSION

The weight-loss curves for $U(C_2O_4)_2 \cdot 2H_2O$ and $U(C_2O_4)_2 \cdot 6H_2O$ are shown in Fig. 1.

The compound, $U(C_2O_4)_2 \cdot 6H_2O$, began to evolve water of hydration at 65°C, giving a break in the curve at 115°C which corresponded approximately to the composition, $U(C_2O_4)_2 \cdot 2H_2O$. Above 115°C further weight loss took place until at 155°C, the composition approached that of $U(C_2O_4)_2 \cdot 1H_2O$. A strictly horizontal

[12] W. W. WENDLANDT, *Analyt. Chem.* **30**, 56 (1958).
[13] W. LODDING and L. HAMMELL, *Rev. Sci. Instrum.* **30**, 885 (1959).
[14] W. LODDING and L. HAMMELL, *Analyt. Chem.* **32**, 657 (1960).
[15] A. H. BLATT, "*Organic Syntheses*," Coll. Vol. 2, p. 414. J. Wiley, New York (1943).
[16] L. E. MARCHI, *Inorganic Syntheses*, (Edited by L. F. AUDRIETH) Vol. 3, p. 166. McGraw-Hill, New York (1950).

weight level was not obtained, however, but the curve does indicate that the 1-hydrate is quite stable thermally. Beginning at about 200°C the 1-hydrate decomposed quite rapidly, giving the UO_3 (containing some U_3O_8) level at 395°C. It is interesting to note that a weight level corresponding to the anhydrous $U(C_2O_4)_2$ was not found, but instead the 1-hydrate, which decomposed directly to the metal oxide. Such behaviour is also known for scandium and the heavier rare-earth oxalates hydrates.[4,5]

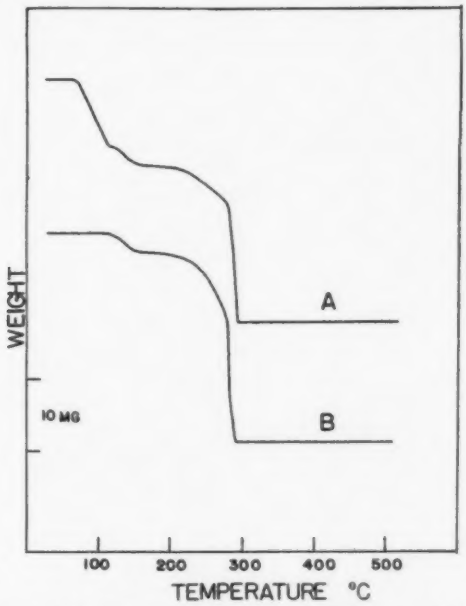

FIG. 1.—Weight-loss curves of the uranium(IV) oxalate hydrates.
A. $U(C_2O_4)_2 \cdot 6H_2O$ B. $U(C_2O_4)_2 \cdot 2H_2O$

The $U(C_2O_4)_2 \cdot 2H_2O$ decomposed in a manner similar to that of the 6-hydrate, after the loss of four moles of water per mole of uranium oxalate. The weight loss temperatures were identical to those found for the 6-hydrate. In contrast to the 6-hydrate, the composition of the oxide level at 395°C corresponded to that for U_3O_8, rather than UO_3.

In Fig. 2, the DTA curves for the two hydrates of $U(C_2O_4)_2$ are given.

For $U(C_2O_4)_2 \cdot 6H_2O$, a prominent endothermic peak was observed at 125°C, followed by two smaller endothermic peaks at 185° and 290°C, respectively. The 125°C peak is presumed (on the basis of weight-loss studies) to be due to the transition:

$$U(C_2O_4)_2 \cdot 6H_2O \rightarrow U(C_2O_4)_2 \cdot 2H_2O + 4H_2O\,(g)$$

while the 185°C peak is assigned to the transition:

$$U(C_2O_4)_2 \cdot 2H_2O \rightarrow U(C_2O_4)_2 \cdot 1H_2O + H_2O\,(g).$$

The 290°C peak probably represents the evolution of the remaining one mole of water and then total disruption of the metal oxalate to the metal oxide or mixture of metal oxides.

The thermal decomposition of $U(C_2O_4)_2 \cdot 2H_2O$ is similar to that found for the 6-hydrate except that the 125°C peak is missing. The two endothermic peaks occurred at 180° and 285°C, respectively.

The DTA curve for $Th(C_2O_4)_2 \cdot 6H_2O$ (Fig. 2) differs from that given by PADMANABHAN *et al.*[2] This may be partly due to the fact that they presumably studied the 2-hydrate instead of the 6-hydrate, or else to the differences in instrumentation. It is a well-known fact that DTA data, unlike infra-red and X-ray data, are not very

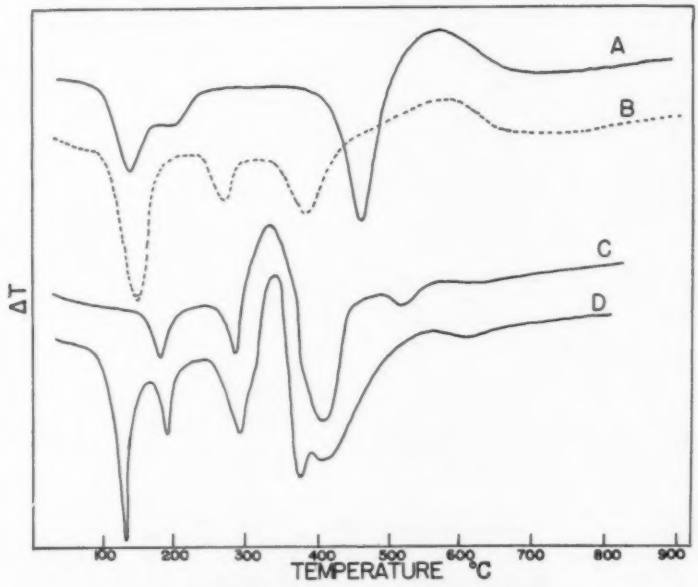

FIG. 2.—DTA curves of metal oxalate hydrates.
A. $Lu_2(C_2O_4)_3 \cdot 6H_2O$ B. $Th(C_2O_4)_2 \cdot 6H_2O$
C. $U(C_2O_4)_2 \cdot 2H_2O$ D. $U(C_2O_4)_2 \cdot 6H_2O$

reproducible due to differences in size and construction material of the sample holders, thermal conductivity of the sample, furnace heating rate, size of thermo-junction, heating rate and so on. However, be that as it may, pronounced differences were found between the DTA curve obtained in this study and that found by the above investigators.

In this investigation, a prominent endothermic peak, centered at 145°C, was found. However, this is about the same peak temperature as was found previously.[2] This peak is presumed to be due to the transition:

$$Th(C_2O_4)_2 \cdot 6H_2O \rightarrow Th(C_2O_4)_2 \cdot 2H_2O + 4H_2O\,(g)$$

while PADMANABHAN *et al.*[2] assigned it to the transition of 2-hydrate → 1-hydrate. It shall later be shown that this is untenable.

Another endothermic peak was found at 270°C, which, on the basis of weight-loss studies (not reproduced), is assigned to the transition:

$$Th(C_2O_4)_2 \cdot 2H_2O \rightarrow Th(C_2O_4)_2 + 2H_2O\,(g)$$

This peak is also present in the previous study[2] but is not very pronounced. The former investigators assigned the peak to the 1-hydrate → anhydrous $Th(C_2O_4)_2$ transition.

The endothermic peak at 385°C and the broad exothermic peak centered at about

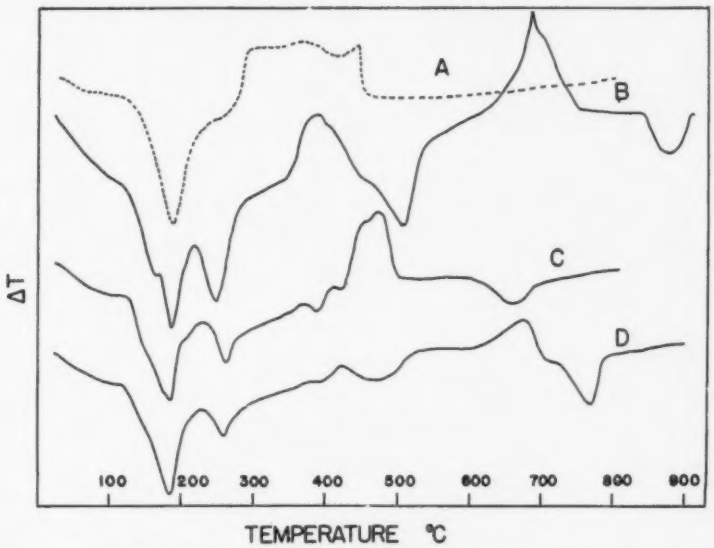

FIG. 3.—DTA curves of rare-earth oxalate hydrates.
A. $Ce_2(C_2O_4)_3 \cdot 10H_2O$ B. $La_2(C_2O_4)_3 \cdot 10H_2O$
C. $Pr_2(C_2O_4)_3 \cdot 10H_2O$ D. $Nd_2(C_2O_4)_3 \cdot 10H_2O$

560°C are assigned to the decomposition of anhydrous $Th(C_2O_4)_2$ to ThO_2. It should be noted that the 385°C peak is not present in the previous work which instead has an exothermic peak beginning at about 370°C.

It appears very doubtful that PADMANABHAN *et al.*[2] were working with pure $Th(C_2O_4)_2 \cdot 2H_2O$ because D'EYE and SELLMAN[1] found that the dehydration of $Th(C_2O_4)_2 \cdot 2H_2O$ took place at 270°C and not 100°C. In this laboratory, it was found that the 2-hydrate began to evolve water at about 250°C, in close agreement with D'EYE and SELLMAN. It appears as though PADMANABHAN *et al.*[2] were studying a higher hydrate, which form their weight-loss curve, was probably a 4-hydrate. The presence of the 4-hydrate could account for the first endothermic peak which began at about 100°C.

The DTA curves for the rare-earth oxalate hydrates are given in Figs. 2–5. In general, all of the endothermic dehydration peaks occurred below 350°C, while the decomposition of the anhydrous metal oxalates, which resulted in both endothermic and exothermic peaks, took place from 350° to 900°C.

In a comparison between the endothermic dehydration peaks below 350°C, the DTA curves of the metal oxalates can be roughly classified according to the same groups as proposed from weight-loss studies,[4] In Group I: lanthanum, praseodymium and neodymium; Group II; samarium, europium, gadolinium and terbium: and Group III: dysprosium, holmium, erbium, ytterbium, thulium and lutetium.

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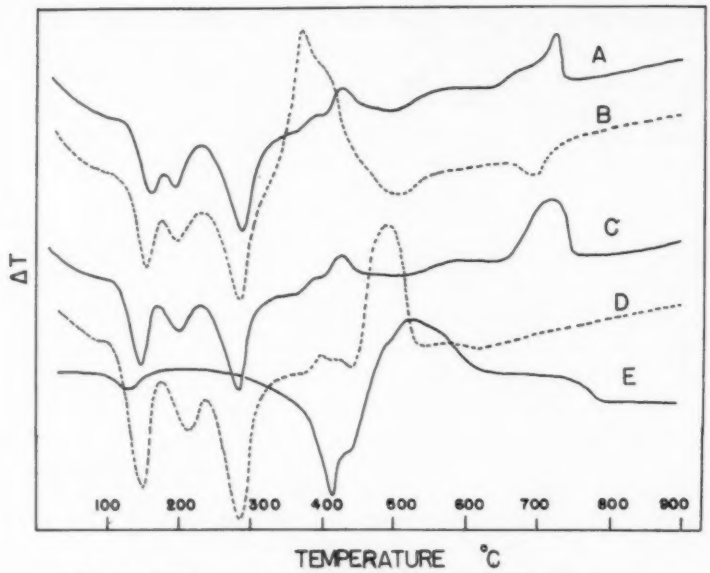

FIG. 4.—DTA curves of scandium and rare-earth oxalate hydrates.
A. $Sm_2(C_2O_4)_3 \cdot 10H_2O$ B. $Eu_2(C_2O_4)_3 \cdot 10H_2O$
C. $Gd_2(C_2O_4)_3 \cdot 10H_2O$ D. $Tb_2(C_2O_4)_3 \cdot 10H_2O$
E. $Sc_2(C_2O_4)_3 \cdot 6H_2O$

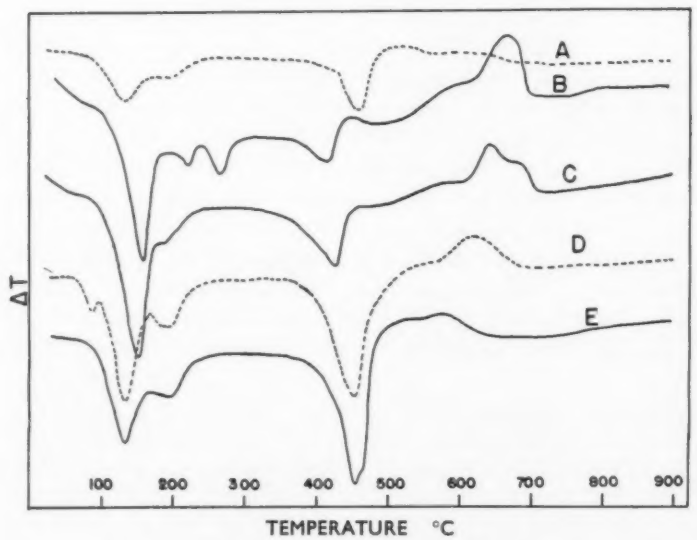

FIG. 5.—DTA curves of rare-earth oxalate hydrates.
A. $Tm_2(C_2O_4)_3 \cdot 5H_2O$ B. $Dy_2(C_2O_4)_3 \cdot 10H_2O$
C. $Ho_2(C_2O_4)_3 \cdot 10H_2O$ D. $Er_2(C_2O_4)_3 \cdot 6H_2O$
E. $Yb_2(C_2O_4)_3 \cdot 5H_2O$

In Group I, weight-loss studies revealed the absence of any intermediate hydrates on going from the 10-hydrate to the anhydrous metal oxalate (at the heating rate employed). In the DTA curves, two prominent peaks were observed, centering at about 185° and 260°C, respectively. Lanthanum had a peak shoulder at about 165°C. The lanthanum curve differed markedly from that given by PADMANABHAN *et al.*[2] However, since they used about seven times the sample size that was employed in this study, the two peaks were probably unresolved into a single peak. The remainder of the curve is also different but this again may be due to a lack of resolution in their instrument.

The Group II oxalates consisted of three endothermic peaks in the 50°–350°C region of the curve. These peaks were centered at about 160°, 200° and 285°C, respectively. From weight-loss measurements,[4] this group contained unstable intermediate hydrates on going from the 10-hydrate to the anhydrous oxalate. It is not possible, due to the complexity of the dehydration reactions, to assign these peaks to definite hydrate transitions.

In the last group, Group III, the dehydration reaction consisted of a main endothermic peak containing either a broad shoulder peak or a smaller peak. This main peak centered about the temperature range, 125°–160°C. Weight-loss measurements[4] revealed the presence of stable intermediate hydrates, usually the 2-hydrate. The anhydrous oxalate was not formed but instead, the 2-hydrate decomposed directly to the metal oxide. This latter reaction appears on the DTA curves as an endothermic peak centered in the temperature range of 415°–460°C. It is the only group that exhibited endothermic peaks in this region of the curve.

All of the peaks beyond 350°C, except in the case of the Group III oxalates, are difficult to interpret. However, the exothermic peaks must certainly represent oxidation reactions of one type or another, since decomposition reactions usually exhibit endothermic heat effects. Praseodymium and terbium exhibited an exothermic peak in the 450°–550°C temperature region which is probably related to the frmation of the oxides, Pr_6O_{11} and Tb_4O_7, respectively. Cerium does not have any peaks beyond about 450°C; however it does exhibit a broad exothermic peak from about 300°–450° which is due to the decomposition of the anhydrous metal oxalate. An explanation for the very pronounced exothermic peaks in the lanthanum and europium oxalate curves is not known.

The DTA curve for scandium oxalate is similar to those for the class III compounds A small endothermic peak at about 125°C and then a much larger peak at 410°C, followed by a broad exothermic peak from 475° to 600°C. This would probably be expected since weight-loss studies[4] showed that the 2-hydrate decomposed directly to the metal oxide, without going through an anhydrous oxalate stage.

The DTA curves of mixtures of the rare-earth oxalates are shown in Fig. 6. In curve A, a 1:1 physical mixture of La–Ce oxalates is presented while in curve B, a 1:1 mixture of La–Ce oxalates that was precipitated by the homogeneous precipitation method. The physical mixture exhibits dehydration endothermic peaks at the appropriate temperatures but the broad exothermic peak from 300° to 450°C is different from the individual lanthanum and cerium oxalate curves. However, the 875°C endothermic peak is still present. The 1:1 precipitated mixture of La–Ce gave only a single endothermic dehydration peak while the broad exothermic decomposition peak began at a slightly higher temperature. The curve was devoid of peaks beyond

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500°C, in contrast to curve A. Curve C is a 1:1 precipitated mixture of Pr–Nd oxalated. The double dehydration peaks are present, although shifted to slightly higher temperatures, while the praseodymium exothermic peak at 460°C has shifted to a

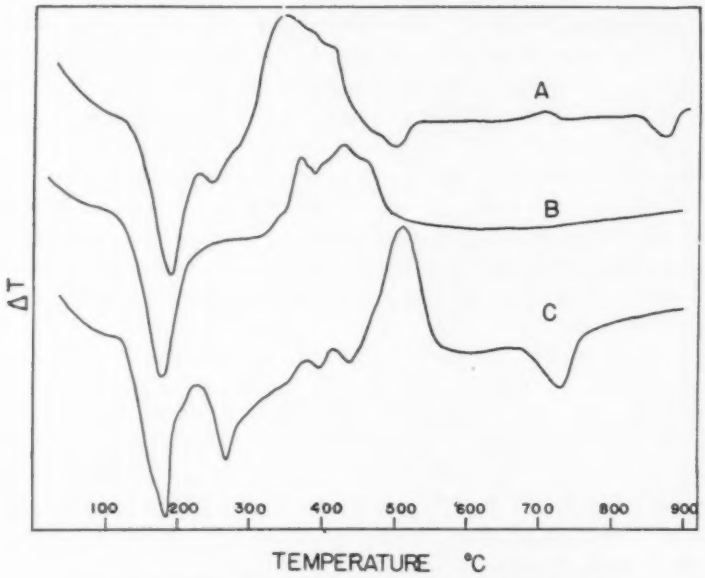

FIG. 6.—DTA curves of rare-earth oxalate hydrate mixtures.
A. 1 : 1 La–Ce oxalate mixture (physical)
B. 1 : 1 La–Ce oxalate mixture (precipitated)
C. 1 : 1 Pr–Nd oxalate mixture (precipitated)

higher temperature, 510°C, in the mixture. In contrast, the 768°C meodymium endothermic peak has shifted to a lower temperature, 670°, while the 675° neodymium exothermic peak has disappeared entirely. It is apparent from the precipitated mixture curves that the resultant curves are not the same as the sum of the curves for the individual oxalates.

Acknowledgement—Partial support of this work by the U.S. Atomic Energy Commission through Contract No. AT-(40-1)-2482 is gratefully acknowledged.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 281 to 285. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF CERIUM (III) NITRATE HYDRATE*

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(*Received* 4 *August* 1960; *in revised form* 26 *September* 1960)

Abstract—The thermal decomposition of cerium (III) nitrate hydrate has been measured in the temperature range $190° < T < 300°C$. Employing information obtained from the infra-red spectra it was found that the decomposition proceeds via the loss of nitrate from the cerium (III) nitrate sample. The composition of the final intermediate decomposition products was measured and discussed.

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THE decomposition of cerium (III) nitrate hydrate was investigated as part of a programme to elucidate the effect of NO_2 in the oxidation of metallic oxides. It was found that the investigation of the thermal decomposition of nitrates yields valuable information regarding the interaction of NO_2 and metallic oxides.[1] In general, it is known that metallic nitrates tend to decompose to either the nitrate, or the oxide, or the metal depending upon the stability of each discrete phase.[2,3,4] It was noted in the thermal decomposition of praseodymium nitrate[1] that the decomposition proceeded via a nitrite intermediate and yielded a non-stoicheiometric oxide as the final reaction product. In conjunction with the work on praseodymium nitrate it was felt desirable to explore the type of decomposition found in the case of the corresponding cerium salt. For this case, it is known that the final oxide resulting from the decomposition of cerium nitrate is the stable phase CeO_2, rather than a non-stoicheiometric material as found in the decomposition of praseodymium nitrate. Thermogravimetric studies carried out by SOMIYA and HIRANO,[5] and WENDLANDT[6] indicate the cerium (III) nitrate hydrate begins to decompose at about 80°C. The decomposition in their study proceeded rapidly at about 280°C and reached a final composition of CeO_2 in the temperature range of 300–400°C. In this previous work[5,6] no other stable intermediate could be identified and dehydration and decomposition seemed contiguous processes.

It was felt necessary to obtain more detailed information regarding the decomposition of cerium (III) nitrate in order to compare the differing mode of oxidation of the cerium ion from a formal charge of Ce(III) to Ce(IV). Thus, the following study was made.

* This research was supported by a subcontract from the Lincoln Laboratories, an organization operated by the Massachusetts Institute of Technology with the joint support of the Army, Navy, and Air Force, AF 19(604)-520, Sub. 208.

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[1] a. F. VRATNY and J. M. HONIG, *Trans. Faraday Soc.* **56**, no. 451, 1051 (1960).
b. F. VRATNY and J. M. HONIG, *J. Chem. Educ.* In Press.
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[3] J. CASES-CASONOVA, *Bull. Soc. Chim. Fr.* 429 (1959).
[4] J. R. PARKS and J. R. PARTINGTON, *J. Chem. Soc.* **72**, 125 (1924).
[5] T. SOMIYA and S. HIRANO, *J. Soc. Chem. Industr., Japan*, Suppl. No. 11, 459B (1931).
[6] W. W. WENDLANDT, *Anal. Chem. Acta* **15**, 435 (1956).

EXPERIMENTAL

The cerium (III) nitrate used in this study was obtained from the G. F. Smith Chemical Company in the form of the 6-hydrate. Because of the method used in the determination of NO_2, it was necessary to dehydrate the hexahydrate as much as posssible. This material was partially dehydrated by vacuum dessication. Further dessication was carried out in the vacuum system. The final hydrate composition preceding decomposition varied between 0·42 and 1·83 mole of water per mole of Ce(III), depending upon the variation in exposure to moist air and extent of evacuation. The method of treating the sample tended to favour the lower value. Further dehydration occurred in the early stages of decomposition. Water was identified by spectroscopic means in the gas phase. The dehydration step and nitrate decomposition could not be completely separated, thus the residual water of hydration was present during the decomposition but was removed before

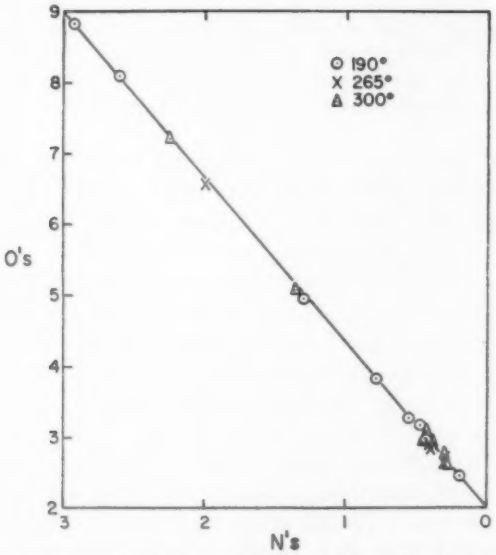

FIG. 1.—Oxygen vs. nitrogen in the decomposition of $Ce(NO_3)_3 \cdot xH_2O$ at three temperatures; (○ ○) 190°C, (× ×) 265°C, (△ △) 300°C. Abscissa: oxygen; Ordinate: nitrogen.

analysis of the sample. Variations in the amount of residual water had no apparent effect upon the rate or mode of decomposition.

The vacuum line used in this study and the method of analysis has previously been described.[1] Briefly, the vacuum line consists of a reaction chamber about 300 cm^3 in volume, a thermocouple-well centred in the reaction vessel and supporting the sample in a crucible. The system further consists of a trap for the condensation of NO_2, a fluorocarbon oil manometer for recording pressures, and pumping facilities.[1b]

Preceding the decomposition the sample of cerium (III) nitrate was evacuated for at least 16 hr at room temperature. This sample was then isolated from the vacuum and thermally decomposed at an appropriate temperature and for a prescribed length of time, to the final composition indicated in Fig. 1. The resultant gases from the decomposition were then discarded, for it had been established that the water arising from the hydrate would interfere with the following gas determinations.

The composition of the decomposition product was established in the following manner. A vacuum was drawn over the sample. The sample was then isolated and further decomposed at a temperature of about 600°C. At this temperature the final solid phase was CeO_2. The NO_2 resulting from the decomposition was condensed at liquid nitrogen temperature in the adjoining trap. The residual gas pressure which was recorded on the oil manometer was taken to be oxygen pressure. The oxygen was removed from the system and the NO_2–N_2O_4 pressure was read on the oil manometer. The amount of O_2 was determined from the total O_2 pressure using the perfect gas law. The amount of

NO_2 was obtained by use of the data of GIAUQUE and KEMP[7]. The summation of these quantities and the final amount of CeO_2 established the composition of the final intermediate decomposition product

In a separate set of runs the samples of cerium (III) nitrate were decomposed as above, however, they were analyzed a bit differently. Instead, the samples were removed from the reaction chamber and the infra-red spectra were taken in Nujol ® mull. Comparison spectra were also taken by the pelleting technique and found to be identical to the Nujol spectra.[8]

RESULTS

The decomposition reactions were carried out within a ten degree range of the following temperatures: 190°, 265°, and 300°C. For the decomposition at 190°C the

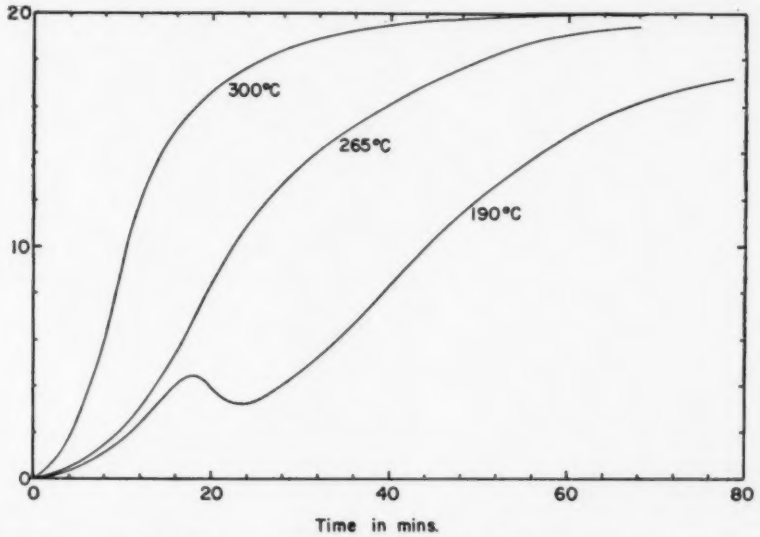

FIG. 2.—Composite kinetic curves for the total pressure as a function of time in the thermal decomposition of $Ce(NO_3)_3xH_2O$. Abscissa: total pressure Ordinate: time in minutes.

total gas pressure resulting from the decomposition was noted to rise as a function of time, then fall slightly, and then rise again (see Fig. 2). For the higher temperatures used in the decomposition a sigmoidal-type curve was noted. It was also noted that the gas resulting in the early stages of decomposition was almost entirely water-vapour, as indicated by the infra-red spectrum of the gas phase, and the fact that this gaseous product was colourless and completely condensable at liquid nitrogen and dry-ice temperatures. An attempt to dehydrate the cerium (III) nitrate via this process failed due to the early inception of the nitrate decomposition. The dip noted in the decomposition curve for the 190°C isotherm is quite probably due to the reaction of H_2O, occurring in the early stages of decomposition and NO_2 visibly occurring at the time of the dip in the curve. The reaction of NO_2 and H_2O can conceivably lead to the formation of HNO_3 and NO and can result in a reduction in pressure. The dip was not resolved in the higher temperature runs, due to the rate of the reaction.

By interrupting the runs at appropriate times it was possible to obtain samples of varying composition. The results are shown in Fig. 1. The ordinate represents the

[7] W. F. GIAUQUE and J. D. KEMP, *J. Chem. Phys.* **6**, 40 (1928).
[8] F. VRATNY, *J. Inorg. Nucl. Chem.* **10**, 328 (1959).

oxygen stoicheiometry of the sample. In all isotherms the oxygen content of the sample decreased linearly with the loss of nitrogen and with the extent of decomposition. Since there is a linear correlation one may infer that the oxidation of Ce(III) to Ce(IV) also occurs linearly with the extent of decomposition.

SPECTRA AND INTERPRETATION

The spectra corresponding to the samples represented by the points in Fig. 1 have been thoroughly examined. It was found that the spectra indicated no perceptible

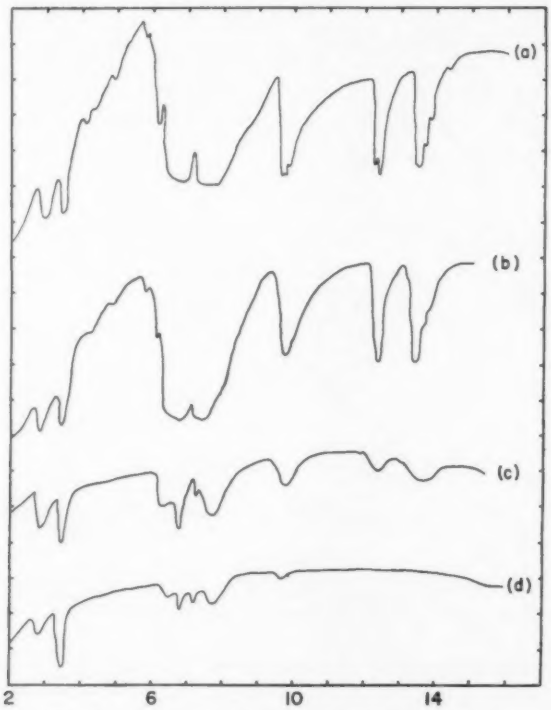

Fig. 3.—Spectra at various stages of decomposition

DECOMPOSITION TIME

Sample spectra	Temp. of decomposition		
	190°	265°	300°
a	20 min	16 min	8 min
b	40 min	24 min	12 min
c	60 min	40 min	20 min
d	140 min	70 min	50 min

Abscissa: % Transmission
Ordinate: Microns

nitrite intermediate in contrast to the decomposition of praseodymium nitrate. The decomposition was noted to proceed with a decrease in relative nitrate present in the sample as indicated by a decrease in the intensity of the nitrate bands. Spectrum a, in Fig. 3, is for a sample in the earliest stages of decomposition which corresponds to the spectrum for a sample decomposed for about eight minutes at 300°C or for about 20 minutes at 190°C. This spectrum is essentially identical with that of cerium (III) nitrate 6-hydrate.[9] As the decomposition proceeds one obtains successively a spectral continuum represented by b, c, and finally d. Spectrum d represents a sample having but a trace of nitrogen.

In the thermal decomposition of cerium (III) nitrate, the nitrate group is retained throughout the path of decomposition which is in sharp contrast to the decomposition of praseodymium nitrate. Thus the oxidation of the central metal ion appears to occur during, or as a result of the actual destruction of the nitrate radical rather than proceeding through several oxidation intermediates as in the case of praseodymium nitrate.

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Acknowledgement—The authors wish to thank Mrs. M. DILLING for obtaining some of the spectra used in this study.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 286 to 294. Pergamon Press Ltd. Printed in Northern Ireland

THE THERMAL DECOMPOSITION OF THE TRIS (ETHYLENEDIAMINE) AND TRIS(1,2-PROPYLENE-DIAMINE) CHROMIUM (III) CHLORIDE AND THIOCYANATE COMPLEXES*

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(*Received* 4 *April* 1960; *in revised form* 30 *August* 1960; *in final form* 11 *October* 1960)

Abstract—The thermal decomposition of the tris(ethylenediamine)-and tris(1,2-propylenediamine chromium(III) chloride and thiocyanate hydrates was studied by thermogravimetric and differential thermal analysis. Three stages of decomposition of the complexes were observed: (a) dehydration; (b) deamination or loss of one mole of amine for each mole of the complex; and (c) total disruption of the complex to Cr_2O_3. The kinetics of the thermal dehydration and deamination was also investigated. The dehydration reactions were first order with E^* values from 12 to 13 kcal. while the deamination reactions ranged in order from 0·4 to 0·9 with E^* values ranging from 18 to 58 kcals. The effect of catalytic amounts of ammonium halides and thiocyanate on the thermal deamination was determined.

PFEIFFER *et al.*[1] found that tris(ethylenediamine)chromium (III) chloride 3·5-hydrate, $[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$, and tris(ethylenediamine)chromium (III) thiocyanate 1-hydrate, $[Cr(en)_3](SCN)_3 \cdot 1H_2O$, evolved water of hydration and ethylenediamine when heated to give *cis*-$[Cr(en)_2Cl_2]Cl$ and *trans*-$[Cr(en)_2[SCN)_2]SCN$, respectively. Further studies by ROLLINSON and BAILAR[2] revealed that the thermal decomposition reactions were catalysed by minute traces of ammonium halide; ammonium chloride for $[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$ and ammonium thiocyanate for $[Cr(en)_3](SCN)_3 \cdot H_2O$. Using these catalysts, they developed a convenient synthesis for the bis-ethylenediamine complexes; the chloride complex was heated at 208–212°C for several hours while the thiocyanate complex was heated at 130°C.

Further studies by O'BRIEN and BAILAR[3] showed that of the tris-ethylenediamine chromium complexes with various anions, only the chloride and thiocyanate thermally deaminated to the bis-ethylenediamine complexes while with the tris-1,2-propylenediamine complexes, only the chloride and thiocyanate exhibited this behaviour. The former gave the bis-1,2-propylenediamine complex at 175°C and the latter at 110°C. In both cases, the decomposition temperatures were somewhat lower than the corresponding ethylenediamine chromium complexes.

Although preliminary studies on the rate of deamination for tris-ethylenediamine chromium complexes have been made,[2] little is known about the thermal decomposition of these complexes. It is thus the object of this investigation to study the thermal

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[1] P. PFEIFFER, P. KOCH, G. LANDO and A. TRIESCHMANN, *Ber. Dtsch. Chem. Ges.* **37**, 4255 (1904).
[2] C. L. ROLLINSON and J. C. BAILAR, *J. Amer. Chem. Soc.* **66**, 641 (1944).
[3] T. D. O'BRIEN and J. C. BAILAR, *J. Amer. Chem. Soc.* **67**, 1856 (1945).

properties of these complexes and also to investigate the kinetics of the dehydration and deamination reactions.

EXPERIMENTAL

Preparations of complexes. The tris(ethylenediamine)- and tris(1,2-propylenediamine)chromium(III) complexes were prepared according to the methods of ROLLINSON and BAILAR[4] and O'BRIEN and BAILAR[5]. Compounds containing minute traces of ammonium halides and thiocyanate as catalysts were prepared by recrystallization of the complexes from 1 per cent solutions of the ammonium salts.

Reagents. The chromium sulphate was obtained from the E. H. Sargent Co., Dallas, Tex. The ethylenediamine and 1,2-propylenediamine were obtained from Eastman Organic Chem., Rochester, N.Y. They were purified by conventional methods and redistilled just before use. All other chemicals used were of C.p. quality.

Thermobalance. The thermobalance used has been previously described.[6] Sample sizes for the kinetic studies ranged in weight from 150 to 175 mg, while for the thermal decomposition studies, 50–150 mg of sample was used. Particle size of the samples used for the kinetic studies was between 200 and 400 mesh. A heating rate of 3·5°C per min was used for the kinetic studies while 5·0°C per min was used for the thermal decomposition studies. All samples were run in duplicate or triplicate with a resulting agreement to each other of about 0·5 per cent on the weight axis and 1 per cent on the temperature axis.

Differential thermal analysis (DTA) apparatus. The DTA apparatus consisted of a furnace similar in design to that previously described by LODDING and HAMMELL[7] and a strip-chart microvolt recorder.[7] Sample sizes ranged in weight from 120 to 150 mg. The samples were finely powdered and packed into the sample chamber by gentle tamping with a glass rod. The top surface of the sample in the sample chamber was covered with a 0·5 cm layer of calcined α-alumina with the same substance being used in the reference chamber. A furnace heating rate of 10·0°C per min. was used with a recorder chart speed of 6 in. per hr. All samples were run in duplicate and in some cases triplicate with resultant agreement between the curves of about 3 per cent (peak maxima temperatures).

RESULTS AND DISCUSSION

Thermal decomposition studies. The thermal decomposition curves, as determined with the thermobalance, of the tris-(ethylenediamine)chromium (III) complexes are given in Fig. 1.

The complex, $[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$ (Curve A), began to lose water of hydration at 40°C, the process being completed at about 180°C. At about 245–255°C, the anhydrous complex began to evolve ethylenediamine, giving a break in the curve at 342°C. This break did not correspond to the complete loss of amine but rather to about 81 per cent of that expected to form the bis-ethylenediamine complex. Additional ethylenediamine was then slowly evolved, with the weight corresponding to that calculated for *c*-$[Cr(en)_2Cl_2]Cl$ being reached at about 380°C. The low yield of the bis-ethylenediamine complex at 342°C may be attributed to the rapid heating rate employed although even at a constant temperature of 208–212°C, only about an 85 per cent yield of this complex was obtained.[2] Beyond 342°C, the complex decomposed to give the Cr_2O_3 weight level, beginning at 580°C.

The thermogram of the bis-ethylenediamine complex, *c*-$[Cr(en)_2Cl_2]Cl$ (Curve B), was similar to that of the above compound beyond 340°C. The first weight-loss was observed at about 340°C, with further rapid decomposition until the Cr_2O_3 weight level was obtained at 580°C.

For the thiocyanate complex, $[Cr(en)_3](SCN)_3 \cdot H_2O$ (Curve C), water of hydration began to come off at a temperature of 40°C, the completely anhydrous complex being

[4] C. L. ROLLINSON and J. C. BAILAR, *J. Amer. Chem. Soc.* **65**, 250 (1943).
[5] W. W. WENDLANDT, *Analyt. Chem.* **30**, 56 (1958).
[6] W. LODDING and L. HAMMELL, *Rev. Sci. Instrum.* **30**, 885 (1959).
[7] W. W. WENDLANDT, *J. Chem. Educ.* **37**, 94 (1960).

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formed at about 130°C. At 220°C, the anhydrous $[Cr(en)_3](SCN)_3$ began to evolve ethylenediamine, and at 280°C, a break in the curve was obtained which corresponded to the complete conversion into *t*-$[Cr(en)_2(SCN)_2]SCN$. Beyond 300°C, further decomposition took place to give the Cr_2O_3 level beginning at 680°C.

The thermobalance curves for the thermal decomposition of the tris(1,2-propylenediamine)chromium(III) complexes are given in Fig. 2.

The two complexes, $[Cr(pn)_3]Cl_3 \cdot 3H_2O$ and *c*-$[Cr(pn)_2Cl_2]Cl$, followed a decomposition pattern similar to that of the corresponding ethylenediamine complexes. The

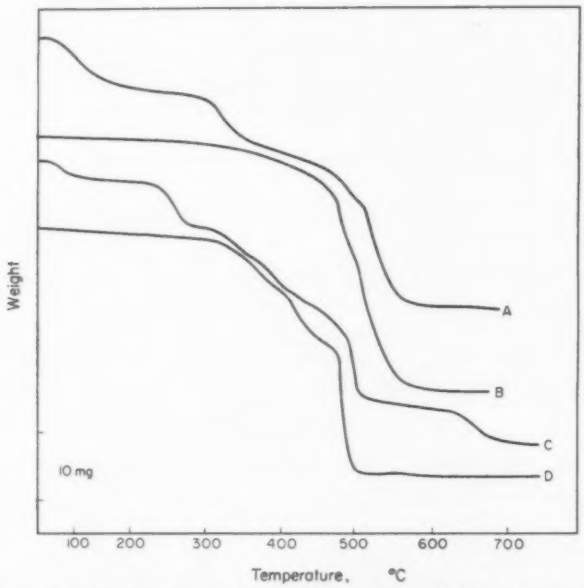

FIG. 1.—Thermogravimetric curves of the tris(ethylenediamine)chromium(III) complexes. Curve A. $[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$; Curve B. *c*-$[Cr(en)_2Cl_2]Cl$; Curve C. $[Cr(en)_3](SCN)_3 \cdot H_2O$; Curve D. *t*-$[Cr(en)_2(SCN)_2]SCN$.

complex, $[Cr(pn)_3]Cl_3 \cdot 3H_2O$ (Curve C), lost water from 40° to 190°C, forming the anhydrous compound, $[Cr(pn)_3]Cl_3$. Above 305°C, the anhydrous complex began to evolve 1,2-propylenediamine to give a break in the curve at 360°C which corresponded to a 70 per cent conversion to $[Cr(pn)_2Cl_2]Cl$. Beyond 360°C, the complex decomposed rapidly to give the Cr_2O_3 level beginning at about 540°C. The thermal decomposition curve for *c*-$[Cr(pn)_2Cl_2]Cl$ (Curve D) showed that the compound was stable from room temperature to 340°C, at which point the complex decomposed rapidly to give the Cr_2O_3 weight-level, beginning at 570°C.

The complex, $[Cr(pn)_3](SCN)_3$ (Curve A), began to evolve 1,2-propylenediamine at 235°C. A break was observed in the curve at 285°C which corresponded to a 71 per cent conversion to the bis-1,2-propylenediamine complex, $[Cr(pn)_2)SCN)_2]SCN$. Beyond 285°C, the complex continued to decompose to give the oxide level, beginning at 710°C. The complex, *t*-$[Cr(pn)_2(SCN)_2]SCN$ (Curve B), did not begin to lose weight until a temperature of 250°C was attained. Above this temperature, the complex decomposed rapidly to give the Cr_2O_3 level, beginning at 680°C.

Differential thermal analysis studies. The DTA curves for the tris(ethylenediamine)chromium(III) complexes are given in Fig. 3.

The complex, $[Cr(en)_3]Cl_3 \cdot 3H_2O$ (Curve A), gave a broad endothermic peak, with a peak shoulder at 125°C and a peak maxima at 145°C. Since this peak was not observed in the anhydrous complex, $[Cr(en)_3]Cl_3$ (Curve B), it must be due to the evolution of hydrate-bound water. Another endothermic peak was then observed at 260°C,

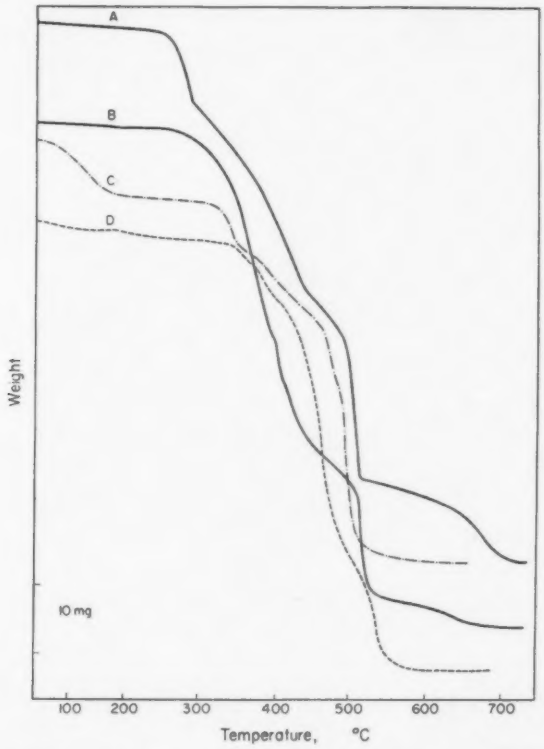

FIG. 2.—Thermogravimetric curves of the tris(1,2-propylenediamine)chromium(III) complexes. Curve *A*. $[Cr(pn)_3](SCN)_3$; Curve *B*. *t*-$[Cr(pn)_3(SCN)_2]SCN$; Curve *C*. $[Cr(pn)_3]Cl_3 \cdot 3H_2O$; Curve *D*. *c*-$[Cr(pn)_3Cl_2]Cl$.

followed by two endothermic peaks with maxima at 325° and 380°C, respectively. The remainder of the curve consisted of a broad exothermic peak extending from about 400° to 600°C. The portion of the curve from 400° to 700°C was not very reproducible due to the voluminous expansion of the complex in the sample chamber as it decomposed to Cr_2O_3. This sample expansion caused the formation of air pockets between the thermocouple and the sample which caused the differential temperature response to be erratic due to changes in the thermal conductivity. The DTA curve for the anhydrous complex was similar to that for the hydrated complex except that the dehydration peak was absent. However, a broad shallow endothermic peak was found from about 80° to 130°C which may be due to traces of water remaining in the complex.

The DTA curve of *c*-$[Cr(en)_2Cl_2]Cl$ (Curve C) was similar to that for the hydrated

and anhydrous tris-ethylenediamine complexes except that the endothermic peak was absent below 300°C. Since the 260°C endothermic peak was not present in the bis-ethylenediamine complex, it is thought that this peak is due to the evolution of ethylenediamine to form the bis-amine complex. Apparently the tris-amine complex deaminates and at the same time introduces two anions into the co-ordination sphere in a one-step process since only one peak was observed. The possibility exists, of course, of one of the peaks masking the other due to the difference in heat evolved or absorbed.

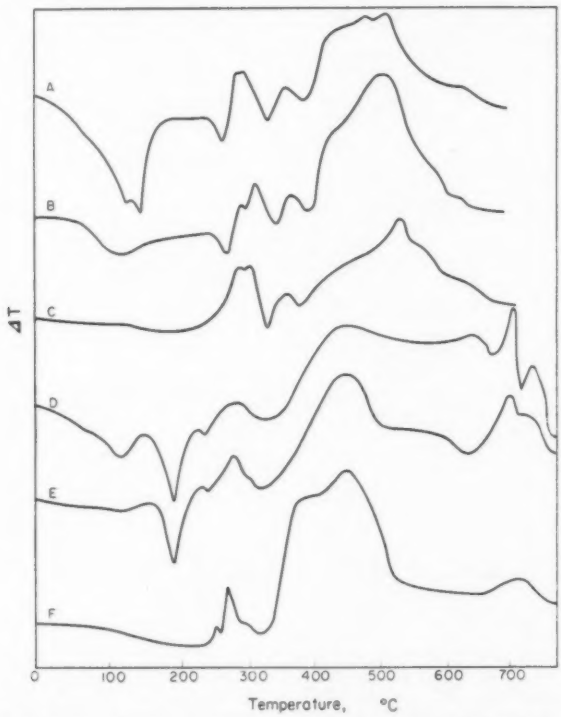

FIG. 3.—DTA thermograms of the tris(ethylenediamine)chromium(III) complexes. Curve A. $[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$; Curve B. $[Cr(en)_3]Cl_3$; Curve C. *c*-$[Cr(en)_3Cl_2]Cl$; Curve D. $[Cr(en)_3](SCN)_3 \cdot H_2O$; Curve E. $[Cr(en)_3](SCN)_3$; Curve F. *t*-$[Cr(en)_2(SCN)_2]SCN$.

For the tris-ethylenediamine chromium thiocyanate complex, $[Cr(en)_3](SCN)_3 \cdot H_2O$ (Curve D), a fairly broad endothermic peak was observed at 120°C, followed by a sharp endothermic peak at 190°C. Since the peak at 120°C was not observed in the curve for the anhydrous complex, $[Cr(en)_3](SCN)_3$ (Curve E), it is presumed to be due to the dehydration reaction. The remainder of the curve consisted of broad exothermic peaks followed by several sharp exothermic peaks beyond 700°C. The anhydrous complex gave a curve which was practically identical to that for the hydrated complex except that the dehydration peak was absent. The bis-ethylenediamine complex, *t*-$[Cr(en)_2(SCN)_2]SCN$ (Curve F), gave a curve which was similar to the curve for the anhydrous complex except that the endothermic peak at 190°C was absent. On the basis of this, the 190°C was assigned to the deamination reaction.

The DTA curves for the tris(1,2-propylenediamine)chromium (III) complexes are given in Fig. 4.

The thermal decomposition curve for $[Cr(pn)_3]Cl_3 \cdot 3H_2O$ (Curve A) exhibited three small endothermic peaks at 95°, 140° and 250°C, respectively. When a comparison is made with the anhydrous complex, $[Cr(pn)_3]Cl_3$ (Curve B), and the bis-amine complex, $[Cr(pn)_2Cl_2]Cl$ (Curve C), it can be seen that the 95° and 140°C peaks are caused by the dehydration reaction and that the 250°C peak is due to the deamination reaction. The remainder of the curves for the above complexes consisted of a number

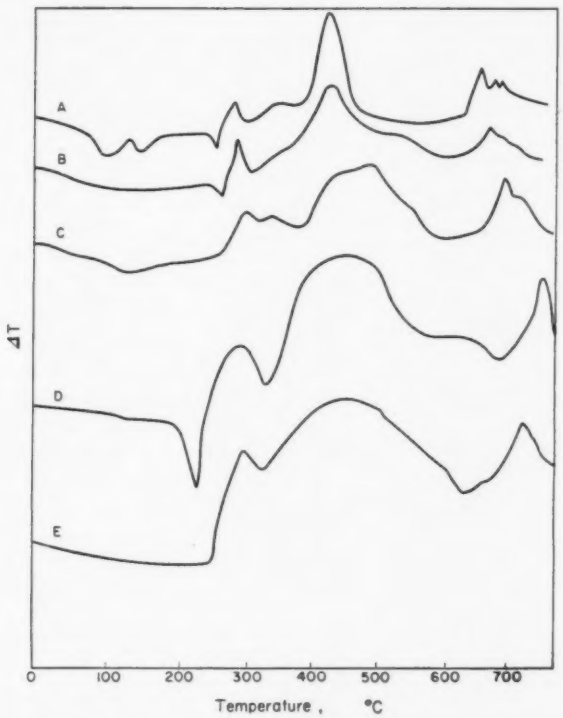

FIG. 4.—DTA thermograms of the tris(1,2-propylenediamine)chromium (III) complexes. Curve A. $[Cr(pn)_3]Cl_3 \cdot 3H_2O$; Curve B. $[Cr(pn)_3]Cl_3$; Curve C. *c*-$[Cr(pn)_2Cl_2]Cl$; Curve D. $[Cr(pn)_3](SCN)_3$; Curve E. *t*-$[Cr(pn)_2(SCN)_2]SCN$.

of exothermic peaks which are related to the further decomposition of the complexes to the metal oxide, Cr_2O_3.

For the tris(1,2-propylenediamine)chromium thiocyanate complex, $[Cr(pn)_3](SCN)_3$ (Curve D), the DTA curve exhibited a rather sharp endothermic peak at 225°C, followed by two broad exothermic peaks and then a sharp exothermic peak at 750°C. The curve for the bis-amine complex, *t*-$[Cr(pn)_2(SCN)_2]SCN$ (Curve E), had the same general shape as the tris-amine complex except that the endothermic peak at 225°C was absent. It can thus be concluded that the 225°C peak is due to the deamination reaction.

Kinetic studies. From a single thermogram, as determined on the thermobalance,

TABLE 1.—KINETICS OF THE THERMAL DECOMPOSITION OF THE CHROMIUM COMPLEXES

Complex	Catalyst	Dehydration		Deamination	
		Order	E_a* (kcal)	Order	E_a* (kcal)
$[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$	none	1·1 ± 0·15	12 ± 1	0·8 ± 0·15	25 ± 2
	NH_4Cl			0·5 ± 0·15	21 ± 2
	NH_4Br			0·6 ± 0·15	21 ± 2
	NH_4I			0·4 ± 0·15	21 ± 2
$[Cr(en)_3](SCN)_3 \cdot 1H_2O$	none	1·1 ± 0·15	13 ± 1	0·7 ± 0·15	34 ± 3
	NH_4Br			0·7 ± 0·15	36 ± 3
	NH_4SCN			0·7 ± 0·15	18 ± 2
	NH_4I			0·7 ± 0·15	36 ± 3
$[Cr(pn)_3]Cl_3 \cdot 3H_2O$	none			0·9 ± 0·15	58 ± 5
	NH_4Cl			0·9 ± 0·15	40 ± 3·5
$[Cr(pn)_3](SCN)_3$	none			0·9 ± 0·15	53 ± 5
	NH_4SCN			0·8 ± 0·15	41 ± 3·5

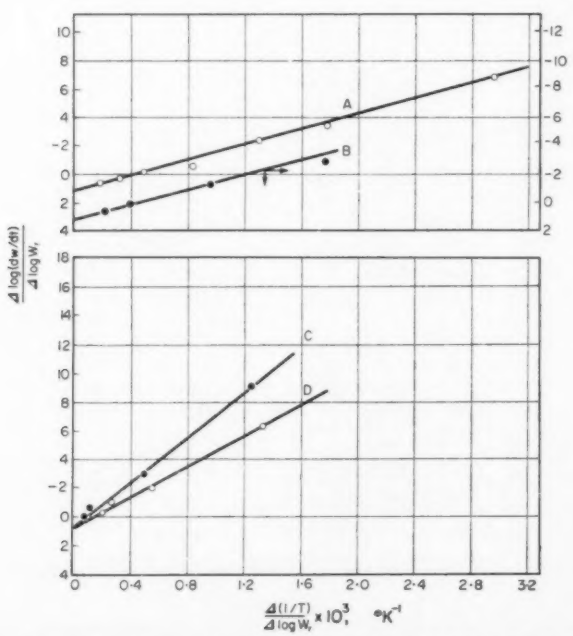

FIG. 5.—Kinetics of the thermal decomposition of the tris(ethylenediamine)chromium(III) complexes. A—dehydration of $[Cr(en)_3]Cl_3 \cdot 3 \cdot 5H_2O$; B—dehydration of $[Cr(en)_3](SCN)_3 \cdot H_2O$; C—deamination of $Cr(en)_3(SCN)_3$ (no catalyst); D—deamination of $[Cr(en)_3]Cl_3$ (no catalyst).

FREEMAN and CARROLL[8] were able to calculate the order of reaction, x, and the activation energy, E^*, by the equation:

$$\frac{-E^*/2{\cdot}3R(1/T)}{\log W_r} = -x + \frac{\log dw/dt}{\log W_r}$$

where $W_r = w_c - w$; w_c is the weight-loss at the completion of the reaction and w is the total loss up to time t.

As applied to this investigation, thermograms were obtained for the tris(ethylenediamine)- and tris(1,2-propylenediamine)-chromium(III) chloride and thiocyanate

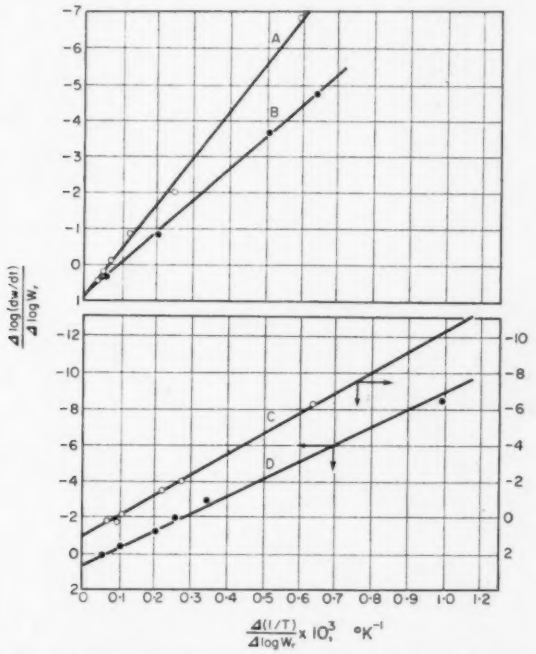

FIG. 6.—Kinetics of the thermal decomposition of the tris(1,2-propylenediamine)chromium(III) complexes. A—deamination of $[Cr(pn)_3]Cl_3$ (no catalyst); B—deamination of $[Cr(pn)_3]Cl_3$ (NH_4Cl catalyst); C—deamination of $[Cr(pn)_3](SCN)_3$ (no catalyst); D—deamination of $[Cr(pn)_3](SCN)_3$ (NH_4SCN catalyst).

complexes in the absence and in the presence of catalytic amounts of ammonium salts. The calculated reaction kinetics for the dehydration and deamination reactions are given in Table 1.

Least square plots of the data for the dehydration and deamination of $[Cr(en)_3]Cl_3{\cdot}3{\cdot}5H_2O$ and $[Cr(en)_3](SCN)_3{\cdot}H_2O$ are given in Fig. 5 while the identical curves for the deamination of the *tris*(1,2-propylenediamine)chromium(III) complexes are given in Fig. 6. While no great accuracy is claimed for these results, the data are illuminating as to the role of the catalysts in the deamination reactions.

For the deamination of $[Cr(en)_3]Cl_3{\cdot}3{\cdot}5H_2O$, the presence of ammonium halides as catalysts lowered the activation energy by only a small amount. It is apparent that

[8] E. S. FREEMAN and B. CARROLL, *J. Phys. Chem.* **62**, 394 (1958).

all of the ammonium halides exhibited similar catalytic effects. The order of reaction averaged about 0·5 for the catalysed samples. This is probably due to the presence of surface effects in the thermal deamination process.

A somewhat different catalytic effect was observed in the case of the deamination of $[Cr(en)_3](SCN)_3 \cdot H_2O$. Ammonium thiocyanate as a catalyst lowered the E^* by about 16 kcal, while the other ammonium halides had little or no effect. All of the deamination reactions were 0·7 order.

For the tris(1,2-propylenedamine)chromium complexes, the corresponding ammonium salt lowered the E^* 18 kcal for the chloride and 12 kcal for the thiocyanate. The order of reaction was 0·9 in all of the reactions but one.

J. Inorg. Nucl. Chem, 1961, Vol. 17, pp. 295 to 301. Pergamon Press Ltd. Printed in Northern Ireland

OXYGEN EXCHANGE BETWEEN CO AND O_2

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(*Received* 11 *August* 1960)

Abstract—The slow reaction of the dried gases CO and O_2 in a quartz vessel, at temperatures below 630°C, is studied with ^{18}O as a tracer. The distribution of ^{18}O isotope between CO, O_2 and CO_2, has been measured. Within the reaction times of the CO–O_2 experiments—from 5 min till 13 hr—there is no measurable oxygen exchange between CO and CO_2, nor between CO_2 and O_2. At the same time there is no measurable oxygen exchange between any of the gases CO, O_2, and CO_2, and the wall of the quartz vessel. CO does not decompose at the wall of the quartz vessel to a measurable extent. From the data it is concluded that, besides the production of CO_2 from CO and O_2, there is an independent oxygen exchange between CO and O_2, without CO_2 production. This exchange has been found to be rapid with regard to the rate of CO_2 production at about 600°C. No exchange has been observed at 395°C. Comparable rates of exchange and rates of CO_2 production have been measured at about 500°C.

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IN a quartz vessel an explosive reaction of the dried gases CO and O_2 is observed at temperatures above 630°C. Below that temperature a slow reaction occurs which is surface-catalysed.[1] In this paper that slow reaction is studied with ^{18}O as a tracer.

The distribution of ^{18}O isotope between CO, O_2 and CO_2 has been measured starting both with ^{18}O enriched CO and natural O_2, and with ^{18}O enriched O_2 and natural CO.

EXPERIMENTAL

Gases

Natural oxygen gas was taken from a gas cylinder obtained from Loos & Co.N. V., purity 99·5 per cent oxygen.

Natural carbon monoxide was prepared according to WEINHOUSE[2] by the reaction of Zn and $CaCO_3$.

The natural gases were enriched by thermal diffusion. Oxygen enriched in this way contained an appreciable amount of argon. The argon was separated from the oxygen by passing the gas mixture through a column of molecular sieves (Linde type 4A), modified by the addition of small amounts of water, at liquid air temperature. The oxygen was sorbed and the argon remained in the gas phase. Excellent separation could be effected.[3]

All gases were purified by keeping the gases for some hours at liquid air temperature.

Apparatus

The reactions were performed in a 30 mm dia. cylindrical transparent quartz vessel, length about 14 cm and volume about 100 cm^3.

The vessels were placed in resistance-heated furnaces. The furnace temperature was maintained constant to $\pm$ 5°C. The temperature gradient along the reaction vessel was less than 10°C. The required vacuum (about 10^{-5} mm mercury) was obtained by a rotary oil and a mercury diffusion pump. The inlet pressure of the gas-mixture was read on a mercury manometer.

(1) B. LEWIS and G. VON ELBE, *Combustion, Flames and Explosions of Gases* Chap. III. Academic Press New York (1951).
(2) S. WEINHOUSE, *J. Amer. Chem. Soc.* **70**, 442 (1948).
(3) R. M. BARRER and A. B. ROBBINS, *Trans. Faraday Soc.* **49**, 807 (1953). D. W. BRECK, W. G. EVERSOLE, R. M. MILTON, T. B. REED and T. L. THOMAS, *J. Amer. Chem. Soc.* **78**, 5963 (1956).

Procedure

The reaction vessel was first baked out for about three days at a temperature 200°C above the reaction temperature. The vessel was heated to the reaction temperature before admitting the gas mixtures. The gases were mixed and subsequently led into the quartz vessel at the desired pressure.

The carbon dioxide from the samples was frozen out in liquid air; in the remaining mixture of CO and O_2, the carbon monoxide was oxidized with iodine pentoxide. This reaction occurs at the surface of the I_2O_5 by heating at about 130°C. In 1 hr nearly 100 per cent can be oxidized. Under these circumstances there is no oxygen exchange between the gas components, nor between each of the gas components and the I_2O_5; there is also no O_2 production by decomposition of I_2O_5. The carbon dioxide formed by the I_2O_5–reaction was frozen out in liquid air, and separated from the remaining O_2. The iodine formed from the I_2O_5 was removed from the CO_2 by condensing the iodine in an aceton–carbon dioxide mixture.

The three components of the samples were analyzed separately by a conventional, 60 degree, mass spectrometer with single collector, constructed in this laboratory.

RESULTS

The results are reported in Tables 1–4. Three reaction vessels have been used. The volumes of the vessels were nearly the same (about 100 cm^3). The volume which was not at the reaction temperature (e.g. the inlet capillary) was always less than 1 per cent.

The production of CO_2 was found by comparing the total pressure of the gas sample and the partial pressure of the CO_2 in the same volume. This quantity—the conversion—is given relatively to the maximum possible production of CO_2. The precision of these pressure readings is 0·1 mm mercury.

F is the relative exchange, or the exchange fraction:

$$F = \frac{x_t - x_0}{x_\infty - x_0},$$

wherein x_t is the fractional content of ^{18}O, in CO or O_2, at time t; x_0 and x_∞ are the values for this fraction at $t = 0$ and $t = \infty$. The recorded values of x_∞ have been calculated from the fractional ^{18}O content and the mixing ratio of the gas components both at $t = 0$. In this calculation, we assumed at $t = \infty$ a proportional distribution of the ^{18}O between the gas components present at $t = 0$. A possible isotope effect was neglected.

The precision of all recorded ^{18}O contents is between 1 and 2 per cent. In experiments 4·1, 4·2 and 4·3, the ^{18}O content of the remaining O_2 has not been measured; the amount was too small for analysis by the mass spectrometer.

The velocity of CO_2 production from CO and O_2, appears to be dependent on the

TABLE 1.—MEASUREMENTS AT 630°C MIXING RATIO CO^*/O_2 EQUAL TO 2:1.
Quartz vessel A, volume 118 cm^3
^{18}O-content CO* 0·675% $x_\infty = 0·438\%$
O_2 0·200%

No.	Pressure (mm)	Time (hr)	Conversion (%)	^{18}O-content (%)		
				CO	O_2	CO_2
1·1	400	1½	14	0·427	0·439	0·417
1·2	400	4	31	0·439	0·445	0·433
1·3	400	8	50	0·435	0·439	0·430
1·4	400	13½	64	0·442	0·443	0·423

TABLE 2.—MEASUREMENTS AT 630°C VARIOUS MIXING RATIOS
Quartz vessel A, volume 118 cm³
Inlet pressure 400 mm mercury

No.	Mixing ratio CO/O_2	Time (min)	Conversion (%)	x_∞	^{18}O-content (%)				
					before		after		
					CO	O_2	CO	O_2	CO_2
2·1	0·25	66	62	0·256	0·700	0·200	0·247	0·252	0·293
2·2	0·50	62	65	0·300	0·700	0·200	0·291	0·293	0·317
2·3	1·00	104	50	0·367	0·700	0·200	0·377	0·365	0·377
2·4	2·00	135	54	0·640	0·200	1·08	0·662	0·647	0·662
2·5	4·00	84	50	0·493	0·200	1·08	0·506	0·508	—

TABLE 3.—MEASUREMENTS AT VARIOUS TEMPERATURES. MIXING RATIO CO^*/O_2 EQUAL TO 2:1
Quartz vessel B, volume about 100 cm³
^{18}O-content CO* 0·790% $x_\infty = 0·495$
O_2 0·200%

Inlet pressure 400 mm mercury $F = \dfrac{x_t - x_0}{x_\infty - x_0}$

No.	Temperature (°C)	Time (min)	Conversion (%)	^{18}O-content (%)			Exchange fraction	
				CO	O_2	CO_2	F_{CO}	F_{O_2}
3·1	625	10	13	0·502	0·477	0·492	1	1
3·2	625	5½	11	0·501	0·497	0·498	1	1
3·3	555	90	35	0·499	0·499	0·504	1	1
3·4	555	20	16	0·517	0·490	0·514	1	1
3·5	465	86	10	0·649	0·335	0·509	0·48 ± 0·07	0·46 ± 0·03
3·6	465	21	4	0·743	—	0·495	0·16 ± 0·06	—
3·7	395	20	—	0·785	0·199	—	0	0

TABLE 4.—MEASUREMENTS AT 470°C AND 500°C. MIXING RATIO CO^*/O_2 EQUAL TO 2:1.
Quartz vessel C, volume about 100 cm³
^{18}O-content CO* 0·635% $x_\infty = 0·418$
O_2 0·200%
Inlet pressure 320 mm mercury

No.	Temperature (°C)	Time (min)	Conversion (%)	^{18}O-content (%)			Exchange fraction	
				CO	O_2	CO_2	F_{CO}	F_{O_2}
4·1	470	30	78	0·597	—	0·414	0·18 ± 0·07	—
4·2	470	50	80	0·565	—	0·412	0·32 ± 0·08	—
4·3	470	70	82	0·549	—	0·413	0·40 ± 0·08	—
4·4	500	30	58	0·552	0·282	0·409	0·38 ± 0·08	0·38 ± 0·03
4·5	500	60	71	0·497	0·348	0·409	0·64 ± 0·08	0·68 ± 0·04

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TABLE 5.—OXYGEN EXCHANGE BETWEEN CO AND CO_2 AT VARIOUS TEMPERATURES
Quartz vessel B

No.	Temp. (°C)	Pressure (mm)		Exchange time (min)	x_∞	^{18}O-content (%)				Exchange fraction F_{CO_2}
						CO		CO_2		
		CO	CO_2			before	after	before	after	
5·1	630	220	150	354	0·450	0·790	0·785	0·200	0·205	0
5·2	820	150	200	173	0·361	0·790		0·200	0·215	0·09 ± 0·03
5·3	850	150	210	153	0·355	0·790		0·200	0·229	0·19 ± 0·03
5·4	900	150	210	144	0·355	0·790		0·200	0·288	0·57 ± 0·06

TABLE 6.—OXYGEN EXCHANGE BETWEEN CO_2 AND O_2 AT VARIOUS TEMPERATURES
Quartz vessel B

No.	Temp. (°C)	Pressure (mm)		Exchange time (min)	x_∞	^{18}O-content (%)				Exchange fraction F_{CO_2}
						O_2		CO_2		
		O_2	CO_2			before	after	before	after	
6·1	630	210	210	302	0·495	0·200	0·198	0·790	0·777	0
6·2	820	220	270	210	0·460	0·780		0·200	0·208	0·03 ± 0·02
6·3	850	240	300	160	0·458	0·780		0·200	0·217	0·07 ± 0·02
6·4	900	250	310	116	0·459	0·780		0·200	0·245	0·17 ± 0·02

TABLE 7.—BOUDOUARD EQUILIBRIUM $2CO \rightleftarrows C + CO_2$ AT VARIOUS TEMPERATURES

	Temperature °K					
	700°	800°	900°	966°	1100°	1200°
K_x	$4 \cdot 10^3$	80	5·0	1·00	$7 \cdot 2 \cdot 10^{-2}$	$1 \cdot 6 \cdot 10^{-2}$
${}_eX_{CO_2}$	0·984	0·895	0·640	0·382	0·06	0·016
${}_eX_{CO}$	0·0158	0·105	0·360	0·618	0·94	0·984

quartz surface and the time of baking out. On the whole the velocity is faster the longer the vessel has been baked out.

No measureable oxygen exchange occurs between any of the purified gases and the wall of the reaction vessels. At 630°C, inlet pressure 250 mm, exchange time 6 hr, there is no change in ^{18}O content for natural, and enriched CO, O_2, or CO_2.

The oxygen exchange between CO and CO_2, and between CO_2 and O_2, is of importance only above 800°C (Tables 5 and 6).

Besides oxidation of CO in the temperature range involved there is a possibility of decomposition at the wall of CO to CO_2 and carbon, leading to the Boudouard equilibrium $2CO \rightleftarrows C + CO_2$. Table 7 reports the equilibrium constant K_x and the related equilibrium mole fractions ${}_eX_{CO_2}$ and ${}_eX_{CO}$ of CO_2 and CO respectively at different temperatures.[4]

(4) G. H. J. BROERS, Thesis, Amsterdam (1958).

At 500°C (773°K) the equilibrium is more than 90 per cent displaced towards the side of CO_2. The time required for establishing equilibrium, or more specifically the decomposition velocity of CO at the walls of the vessels is important.

We admitted CO to the reaction vessels at 500°C and at 535°C, inlet pressure 320 mm, reaction time 5 hours; a measurable production of CO_2 was not observed. There is no striking difference in reaction velocity at 500°C, for mixtures of $CO/O_2/CO_2$ and $CO/O_2/N_2$ with mixing ratios equal to 2:1:18. (Table 8).

TABLE 8.—COMPARATIVE EXPERIMENTS AT 500°C. MIXTURES $CO/O_2/CO_2$ AND $CO/O_2/N_2$ WITH MIXING RATIO EQUAL TO 2:1:18
Quartz vessel C
Inlet pressure 500 mm mercury

No.	Mixtures with mixing ratio equal to 2:1:18	Reaction time (min)	Conversion (%)		
			Experiment no.		
			1	2	3
8·1	$CO/O_2/CO_2$	17½	69	59	58
8·2	$CO/O_2/N_2$	17½	60	60	62

In none of our experiments has carbon deposition been observed. There is no measurable oxygen exchange between CO and CO_2 at 500°C: experiments with mixing ratio CO/CO_2 equal to 1:1, inlet pressure 410 mm, exchange time 2 hr, showed no change in ^{18}O-content of CO and CO_2. Thus no evidence has been found for CO decomposition at the walls of the reaction vessels.

DISCUSSION

Within the reaction times mentioned in the tables, at 630°C and below there is no measurable oxygen exchange between CO and CO_2, or between CO_2 and O_2. In the same time there is no measurable oxygen exchange between the gases and the wall of the quartz vessel. It has been shown that CO does not decompose, according to the Boudouard mechanism, at the walls of the quartz vessels to a measurable extent. With this in mind, it seems justified to conclude from the data in Tables 1–4, that besides production of CO_2 from CO and O_2, independently there is an oxygen exchange between CO and O_2, without CO_2 production.

At about 630°C (experiments 1·1, 1·2, 1·3, 1·4 and 3·1, 3·2) for the stoicheiometric mixing ratio, the oxygen exchange between CO and O_2 is rapid with regard to the rate of CO_2 production. After 5½ min (experiment 3·2) the ^{18}O content of the remaining CO and O_2 corresponds to the value of x_∞ calculated at $t = 0$.

In Table 2, besides an experiment with the stoicheiometric mixing ratio, some experiments with different ratios are reported. In these experiments the mixing ratio changes with time in consequence of the CO_2 production, and so does the value of x_∞. If the exchange is slow with regard to the CO_2 production, in experiments 2·1, 2·2, 2·3, and 2·5, the ^{18}O content at equipartition would be lower than the value of x_∞ calculated at $t = 0$. However, the ^{18}O content of the remaining CO and O_2, in these experiments at 630°C, practically corresponds to the value of x_∞ calculated at $t = 0$. Thus the oxygen exchange between CO and O_2 is rapid with regard to the CO_2 production.

Table 3 reports a number of experiments with the stoicheiometric mixing ratio at various temperatures between 625°C and 395°C. The eighth and ninth columns of Table 3 mention F_{CO} and F_{O_2}, the exchange fraction respectively with regard to CO and O_2. At 625°C and 555°C the ^{18}O is equipartitioned among CO and O_2 within the reported time ($F = 1$). No exchange is observed at 395°C ($F = 0$). At 465°C the exchange velocity is easily measurable ($0 < F < 1$).

In Table 4 some experiments with stoicheiometric gas mixtures in a third quartz vessel are added. At 470°C (experiments 4·1, 4·2 and 4·3) a marked increase of the exchange fraction with time has been observed, while there is only a slight increase in CO_2 production. In all experiments performed as in experiments 3·5, 4·4 and 4·5, the exchange fractions F_{CO} and F_{O_2} for one experiment agree within experimental error. So the relative amount of ^{18}O in CO and O_2 together does not change.

At least at about 600°C the reaction between CO and O_2 probably proceeds by way of oxygen atoms.[1,5,6] KNIPE and GORDON,[5] in their experiments at 600°C, observe a rapid reaction between CO and O_2 in the first minutes, and after that a slow one. HARTECK and DONDES[6] attribute this fast induction period to production of suboxides reacting with O-atoms in a chain mechanism. Consumption of O-atoms without branching will build up a steady state and the reaction is slowed down.

In our experiments 2·1, 2·2 and 2·3 a fast initial reaction may produce CO_2, from CO and O_2 with ^{18}O not yet equipartitioned. If we assume the reaction occurs between CO and O-atoms, in the experiments mentioned one will expect CO_2 with ^{18}O content greater than the value of x_∞. Indeed, the ^{18}O content of CO_2 in experiments 2·1, 2·2, and 2·3 does exceed the related value of x_∞.

The oxygen exchange between CO and O_2 can be correlated with the reaction scheme for the slow reaction between CO and O_2 at 600°C, suggested by HARTECK and DONDES.[6] According to these authors a suboxide is formed by collision of a CO molecule with excess energy, and a normal CO molecule, producing an O atom. On the other hand a suboxide may decompose by reaction with an O atom, producing CO again.

$$CO + O + CO \rightarrow CO_2 + CO^*$$
$$CO^* (5{\cdot}5\ eV) + CO \rightarrow C_2O + O$$
$$C_2O + CO + M \rightarrow C_3O_2 + M \qquad (M \text{ is a third body})$$

and

$$C_2O + O \rightarrow 2CO$$
$$C_3O_2 + O \rightarrow 3CO$$

The oxygen exchange between CO and O_2 is however, explained more simply in the basic scheme of LEWIS and VON ELBE.[1]

$$O + CO + M \rightarrow CO_2^* + M \qquad (1)$$

and

$$CO_2^* + M \rightarrow CO + O + M \qquad (2)$$

with besides (2) the reactions

$$CO_2^* + M \rightarrow CO_2 + M$$
$$CO_2^* + O_2 \rightarrow CO_2 + 2O$$
$$CO_2^* \rightarrow CO_2 + h\nu$$

[5] A. S. GORDON and R. H. KNIPE, *J. Chem. Phys.* **27**, 1418 (1957).
[6] P. HARTECK and S. DONDES, *J. Chem. Phys.* **27**, 1419 (1957).

GORDON and KNIPE[7] conclude from a qualitative construction of the potential energy surfaces, that the bimolecular collision of CO and O probably should be effective in producing excited states of the CO_2 molecule with lifetimes long enough to be of kinetic significance. Thus besides the reactions of LEWIS and VON ELBE one gets

$$CO + O \rightarrow CO_2^*$$

and

$$CO_2^* \rightarrow CO + O$$

which would also effect oxygen exchange.

Acknowledgements—We are indebted to Professor Dr J. A. A. Ketelaar for discussions and helpful suggestions. We also thank Professor Dr J. Kistemaker for his stimulating interest.

This work is part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental Research of Matter) and has been made possible by financial support from the Foundation Z.W.O. (Netherlands Organisation for Pure Scientific Research).

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THE USE OF THE HAMMETT ACIDITY FUNCTION, H_0, FOR ESTIMATING THE HYDROGEN ION CONCENTRATION IN ACIDS

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(*Received* 8 *June* 1960)

Abstract—A method is described where the hydrogen ion concentration in acid solutions is evaluated from H_0-data. For CF_3COOH, good agreement is found between this and the NMR methods below 6 M. For the acids HF, $CH_2ClCOOH$ and $CHCl_2COOH$, pK-values in rather good agreement with those in the literature are obtained. Application to HCl and HBr gives the following tentative K-values for these acids:

$$1{\cdot}05 < \log K_{HCl} < 2{\cdot}60; \qquad 2{\cdot}15 < \log K_{HBr} < 4{\cdot}65$$

Only upper and lower limits can be given for K because of the difficulty in making a sound extrapolation to pure water. It has also been found that, because of a large variation of the activity coefficient of the undissociated acid, Raoult's law cannot be used for estimating its concentration in aqueous solutions of strong acids.

RECENTLY WYATT[1a] as well as BASCOMBE and BELL[1b] have shown how acidity functions can be used for estimating the degree of dissociation, α in acid solutions. In the following, a slightly different approach to the same problem will be described and applied to a number of different acids.

METHOD

The Hammett acidity function, H_0, is related to the activity of *free* unhydrated protons, a_{H^+}, by:[2]

$$\log \varphi\, a_{H^+} = -H_0 \tag{1}$$

where

$$\varphi = y_B/y_{BH^+} \tag{2}$$

φ is the ratio of the activity coefficients on the molarity scale of the basic form, B, and conjugate acid, BH^+, of the indicators used for measuring H_0. Introducing the stoicheiometric molarity activity coefficient, y'_{H^+} of H^+ we get from (1)

$$\log \varphi y_{H^+} + \log C_{H^+} = -H_0 \tag{3}$$

For a monobasic acid, HA, which dissociates into H^+ and A^-, α is defined by:

$$C_{H^+} = C_{A^-} = \alpha C \tag{4}$$

where C is the stoicheiometric molarity of acid.

Equation (3) can be used for estimating C_{H^+} provided the function φy_{H^+} is known. Concerning φ it is generally accepted for solutions of strong acids in water that, at any given concentration, φ is independent of the indicator used.[3] This assumption has recently found a striking confirmation. When plotting H_0 vs. a_{H_2O} for HNO_3, HCl, H_2SO_4 and $HClO_4$, WYATT[1a] found that all data fell on a single curve. Also HBr follows the same curve.[4] This behaviour implies that, when compared at the same water activity, φ as well as the hydration equilibria of the proton are the same in all these different acids.[1a,4]

In Fig. 1, $\log \varphi y_{H^+}$ is plotted vs. H_0 for three acids: HNO_3, $HClO_4$ and H_2SO_4. The experimental

(1) (a) P. A. H. WYATT, *Disc. Faraday Soc.* **24**, 162 (1957). (b) K. N. BASCOMBE and R. P. BELL *Ibid.* 158 (c) O. REDLICH and G. C. HOOD., *Ibid.* 87.
(2) L. P. HAMMETT, *Physical Organic Chemistry* p. 267 McGraw-Hill New York (1940).
(3) M. A. PAUL and F. A. LONG, *Chem. Rev.* **57**, 1 (1957).
(4) E. HÖGFELDT, *Acta Chem. Scand.* **14**, 1627 (1960).

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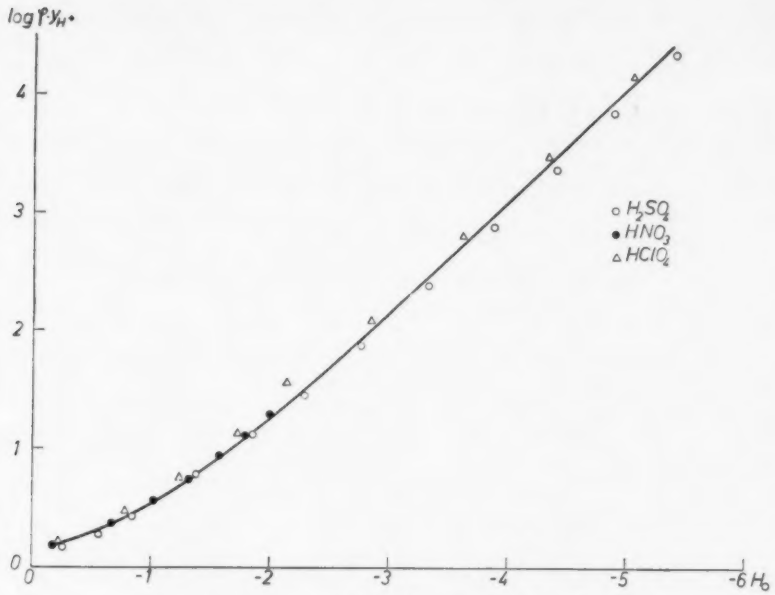

FIG. 1.—log $\varphi_{H^+}y$ vs. H_0 for: ● HNO_3 △ $HClO_4$ ○ H_2SO_4.

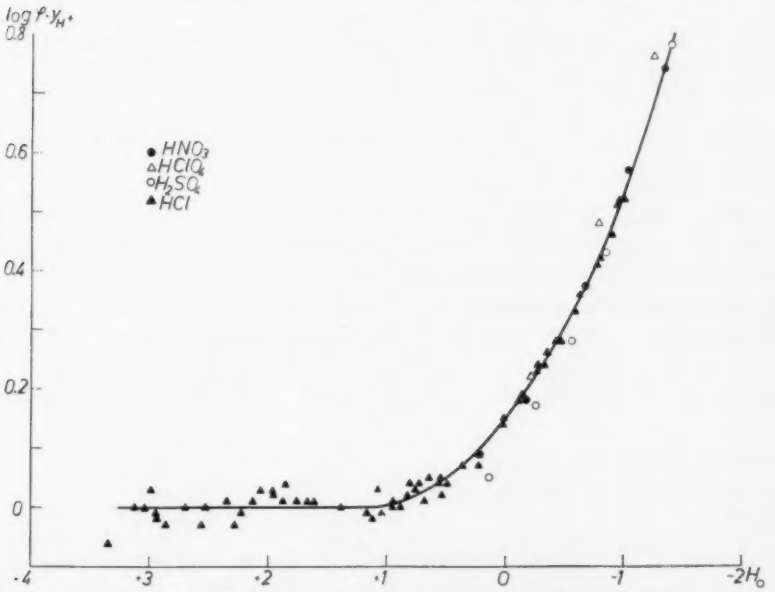

FIG. 2.—log $\phi\, y_{H^+}$ vs. H_0 in relatively dilute solutions for: ● HNO_3 △ $HClO_4$ ○ H_2SO_4 ▲ HCl.

data are those used in ref 4. As may be seen, all the data fall on a single curve within the limits of experimental error, which can be estimated to be around $\pm 0{\cdot}05$. This behaviour is in agreement with WYATT's finding.

In dilute solutions, φy_{H^+} approaches unity because pure water is here taken as the reference state for all activity coefficients and H_0 will therefore approach $-\log C_{H^+}$. In Fig. 2, $\log \varphi y_{H^+}$ is plotted vs.

H_0 for relatively dilute solutions. The HCl data are those of HÖGFELDT.[5] As shown in a later section, HCl is likely to be completely dissociated below 3 M i.e. for $H_0 > -1$. As seen in Fig. 2, $\log \varphi y_{H^+} \approx 0$ for $H_0 > +1$ i.e. for $C < 0{\cdot}1$ M. This may have the following reasons (a) a cancellation of the electrostatic interactions on H^+ and BH^+ and (b) the water activity varies too little to cause any appreciable displacement of the hydration equilibria.

In the following we shall assume as a *working hypothesis* that φy_{H^+} is the same function of H_0 for all acids as is indicated in Figs. 1 and 2 and evaluate C_{H^+} from equation (3). It would be expected, however, that for relatively weak acids where the dielectric constant attains low values in concentrated solutions, ion pair formation involving the indicator ions will cause individual variations in φ and the above assumption will break down.[3]

TABLE 1.—THE FUNCTION $\log \varphi y_{H^+}$ FOR ROUND H_0-VALUES

H_0	$\log \varphi y_{H^+}$	H_0	$\log \varphi y_{H^+}$
>1	0	−2·00	1·30
+0·75	0·02	−2·50	1·70
+0·50	0·05	−3·00	2·15
+0·25	0·09	−3·50	2·62
0	0·15	−4·00	3·10
−0·25	0·22	−4·50	3·56
−0·50	0·30	−5·00	4·04
−0·75	0·41	−5·50	4·52
−1·00	0·53	−6·00	4·98
−1·50	0·85		

In Table 1 average values for $\log \varphi y_{H^+}$ are tabulated for round H_0-values. They are collected from the best Raman and Nuclear Magnetic Resonance (NMR) data available to the present writer. They will need revision when a body of more complete and more accurate data has been assembled.

APPLICATIONS

(a) *Weak and moderately strong acids*

In the following the method outlined in the previous paragraph has been used for finding the thermodynamic dissociation constants of some acids, and the results are compared with the values in the literature.

The thermodynamic dissociation constant is obtained by extrapolation of some suitable function to infinite dilution. Two different functions have frequently been used, the stoicheiometric dissociation constant, Q, or the function Ky_{HA}, where y_{HA} is the activity coefficient of undissociated acid. These two functions will now be discussed.

For the reaction:

$$HA \rightleftarrows H^+ + A^- \tag{5}$$

Q is given by

$$Q = \frac{C_{H^+}C_{A^-}}{C_{HA}} = \frac{C\alpha^2}{1-\alpha} = \frac{Ky_{HA}}{y_{H^+}y_{A^-}} \tag{6}$$

Since all activity coefficients approach unity upon dilution, the extrapolated Q-value will give the thermodynamic dissociation constant, K. Analogously we find from (6):

$$Ky_{HA} = \frac{a_{H^+}a_{A^-}}{C(1-\alpha)} \tag{7}$$

[5] E. HÖGFELDT and J. BIGELEISEN, *J. Amer. Chem. Soc.* **82**, 15 (1960).

where the activity product $a_{H^+}a_{A^-}$ can be computed from stoicheiometric mean activity coefficients tabulated in the literature.

It is known that for most strong electrolytes activity coefficient products like $y_{H^+}y_{A^-}$ have a minimum near 1 M. On the other hand one would expect y_{HA} to follow a function.

$$\log y_{HA} = kC \tag{8}$$

where the constant k is called the salting out constant. This implies that Q might go through a maximum making any extrapolation of Q most uncertain. The possible behaviour of Q can be illustrated by the following example.

$$\text{Assume: } \log y_{HA} = 0{\cdot}05C \log y_{H^+} = \log y_{A^-} = -\frac{1}{2}\cdot\frac{\sqrt{c}}{1+\sqrt{c}} + 0{\cdot}1C \tag{9a, b}$$

where 0·05 is a typical value for the salting out constant of a non-electrolyte[6] and 0·1 a typical value for an electrolyte.[7] Inserting (9) into (6), differentiation yields:

$$Q_{max} \text{ for } C \approx 0{\cdot}83 \text{ M} \tag{10}$$

On the other hand, a maximum in the extrapolation path for Ky_{HA} is not likely to appear and this function should always be preferred whenever good activity data are available. Unfortunately, such data are lacking for several of the acids for which H_0 has been measured, so at present it is necessary to resort to the Q-extrapolation in most cases.

For CF_3COOH a direct comparison can be made between NMR[8] and H_0 measurements.[9] The NMR measurements give directly the α-values while the H_0 method employs equation (3) and the data in Table 1. In Fig. 3, α from the two sets of measurements are compared. When evaluating α from the H_0 data of RANDLES and TEDDER the measurements for the two indicators *o*-nitroaniline and 4-chloro-2-nitroaniline have been used with the pK-values —0·29 and —1·03 as recommended by PAUL and LONG[3] and in good agreement with recent measurements.[5,10] The densities necessary for transformation from the mole fraction scale used by RANDLES and TEDDER to the molar scale were determined by the present writer in connection with some NMR measurements.[11] The latter show good agreement with those of REDLICH *et al.*[8] below 10 M. From Fig. 3 it is seen that there is rather good agreement up to 6 M. Above that concentration deviations start to occur which are probably an example of a failure of the working hypothesis due to ion pair formation involving the indicator ions.[3] With knowledge of α and the mean activity of acid the function Ky_{HA} can be computed and extrapolated to $C = 0$ in order to give a value for K. When doing so the activities of CF_3COOH-solutions used were the same as those of REDLICH *et al.*[8] The agreement between $K_{NMR} = 1{\cdot}8$ and $K_{H_0} = 1{\cdot}4$ is encouraging in view of the experimental uncertainty in H_0 and the crude treatment of the NMR-data.

For the other acids where no direct comparison can be made, Q has been computed from (6) and in Fig. 4 log Q is plotted vs. C for these acids. In Table 2 the pK-values obtained are compared with the literature.

[6] F. A. LONG and W. F. MCDEVIT, *Chem. Rev.* **51**, 119 (1952).
[7] C. W. DAVIES, *J. Chem. Soc.* 2093 (1938).
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[10] K. N. BASCOMBE and R. P. BELL, *J. Chem. Soc.* 1096 (1959).
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For H_3PO_3 and H_3PO_4, H_0 has not been determined in sufficiently dilute solutions to permit any reasonably good extrapolation. For H_3PO_3 the measurements in very dilute solutions by KOLTHOFF[18] are also marked in Fig. 4 and they seem to

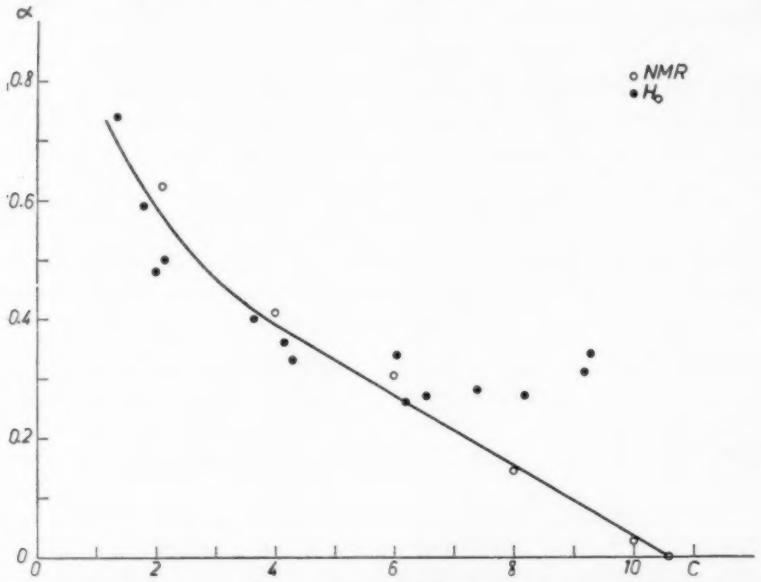

FIG. 3.—The degree of dissociation, α, for CF_3COOH vs. stoicheiometric molarity of acid. ○ NMR-data, ● H_0-data.

TABLE 2.—pK-VALUES FROM H_0-DATA COMPARED WITH THE LITERATURE. $t = 25°C$

Acid	Symbol in Fig. 4.	H_0-data Ref	p$K(H_0)$	pK(Lit)	Lit Refs
$CH_2ClCOOH$	■	10	2·8	2·86	12
HF*	□	3	3·1	2·91–3·27	13, 14, 15
H_3PO_4	△	3, 16	—	2·12	17
H_3PO_3	◑	10	—	1·70–1·80	18, 19
$CHCl_2COOH$	▲	10	1·1	1·06	3
CCl_3COOH	●	10, 20	—	0·64	21
CH_3SO_3H	○	10	−1·1	−0·6	10

* When evaluating Q for HF the value $K = 4$ for the reaction

$$F^- + HF \rightleftarrows HF_2^- \qquad (11)$$

was employed.[13–16]

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[20] H. BURKETT, R. MURPHY and D. YARIAN, *Indiana Acad. Sci.* **66**, 86 (1957).
[21] O. REDLICH, *Chem. Rev.* **49**, 333 (1946).

fit well into the H_0-data. For CCl_3COOH log Q must have a maximum if the present literature value is accepted as correct. This illustrates the possible drawback of the log Q-plot pointed out earlier.

For CH_3SO_3H the value $K = 4$, suggested in the literature, was estimated from H_0-data by BELL[10] and offers no independent check. The discrepancy between $K = 4$ and the present estimate of $K \sim 10$ from the same data is likely to be due to the different approximations inherent in the two approaches.

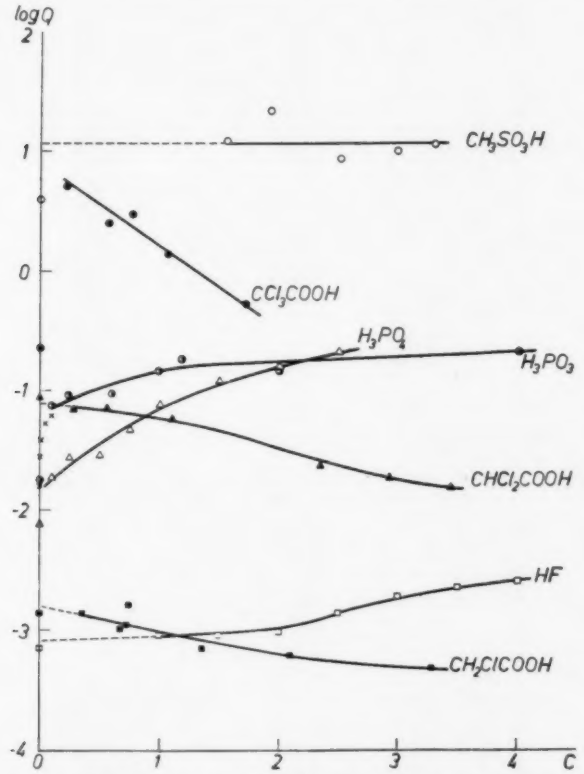

FIG. 4.—The function log Q vs. the stoicheiometric molarity of acid for: ○ CH_3SO_3H ● CCl_3COOH, ◑ H_3PO_3, × H_3PO_3 (Kolthoff), △ H_3PO_4, ▲ $CHCl_2COOH$, □ HF, ■ $CH_2ClCOOH$.

For the acids H_3PO_3, CCl_3COOH and CH_3SO_3H, α was found to become constant, or to increase at about 7·5, 5 and 9 M respectively. These results indicate that at high concentrations the method of estimating α from H_0 measurements is not applicable as found for CF_3COOH above 6 M. When good activity measurements are available, the plot of φa_{H^+} vs. a_{H_2O} will provide a criterion for each acid of how far this method of estimating α can be applied.

(b) *The strong acids* HCl *and* HBr

For HCl, Raman methods have indicated measurable amounts of HCl molecules at 9 M[22] and analogous conclusions have been drawn from NMR measurements of

[22] L. OCHS, I. GUÉRON and M. MAGAT, *J. Phys. Rad.* 1, 85 (1940).

HCl, HBr and HI.[23] Since H_0-measurements exist for HCl and HBr and the curve of H_0 vs. a_{H_2O} is the same for these two acids as for HNO_3, $HClO_4$ and H_2SO_4, it may be legitimate as a first approximation to use the data in Table 1 even in concentrated solutions in contrast to the weak acids discussed in the preceding paragraph. The H_0 data used are those given in the review by PAUL and LONG[3] together

TABLE 3.—TENTATIVE α-VALUES FOR HCl FROM EQUATIONS (3) AND (4)

C_{HCl}	H_0	$\log \varphi y_{H^+}$	$\log \alpha$	α
1	−0·20	0·20	0	1
2	−0·69	0·38	+0·01	~1
3	−1·05	0·57	0	1
4	−1·40	0·82	−0·02	0·96
4·5	−1·58	0·96	−0·03	0·93
5	−1·76	1·10	−0·04	0·91
5·5	−1·93	1·23	−0·04	0·91
6	−2·12	1·39	−0·05	0·89
7	−2·56	1·76	−0·05	0·89
8	−2·86	2·03	−0·07	0·85
9	−3·22	2·35	−0·08	0·83
10	−3·59	2·71	−0·12	0·76
11	−3·99	3·08	−0·13	0·74
12	−4·41	3·48	−0·15	0·71
13	−4·82	3·87	−0·16	0·69

TABLE 4.—TENTATIVE α-VALUES FOR HBr FROM EQUATIONS (3) AND (4)

C_{HBr}	H_0	$\log \varphi y_{H^+}$	$\log \alpha$	α
0·1	0·98	0	+0·02	~1
0·5	0·20	0·10	0	1
1	−0·20	0·20	0	1
2	−0·71	0·39	+0·02	~1
3	−1·11	0·60	+0·03	~1
4	−1·50	0·89	+0·01	~1
5	−1·93	1·23	0	1
6	−2·38	1·60	0	1
7	−2·85	2·02	−0·02	0·96
8	−3·34	2·47	−0·03	0·93
9	−3·89	2·98	−0·04	0·91
10	−4·44	3·50	−0·06	0·87

with those of HÖGFELDT[5] for dilute solutions of HCl. The resulting α-values are given in Tables 3 and 4. These α-values can only be regarded as tentative because $\log \alpha$ is obtained as a difference between two rather uncertain numbers. Since no other estimates of α in these acids seem to exist, no direct comparison can be made. The NMR measurements of REDLICH *et al.*[24] can be used for a consistency test. From proton resonance measurements α is currently computed from

$$S/p = S_1\alpha + S_2(1 - \alpha) \tag{12}$$

[23] Y. MASUDA and T. KANDA, *J. Phys. Soc. Japan* **9**, 82 (1954)
[24] G. C. HOOD, O. REDLICH and C. A. REILLY, *J. Chem. Phys.* **22**, 2067 (1954)

where S is the corrected resonance shift and p is a function of the stoicheiometric mole fraction of acid, X, defined by:

$$p = \frac{3X}{2 - X} \tag{13}$$

S_1 and S_2 are two empirical constants, which thus have to be evaluated from the experiments. By extrapolation to pure water, REDLICH *et al.*[24] found the following value for S_1:

$$S_1 = 11{\cdot}43 \tag{14}$$

For S_2 no value has been obtained because it requires knowledge of the dissociation in some reference solution, which is difficult to get for HCl because pure HCl is not available at the ordinary temperature and pressure.

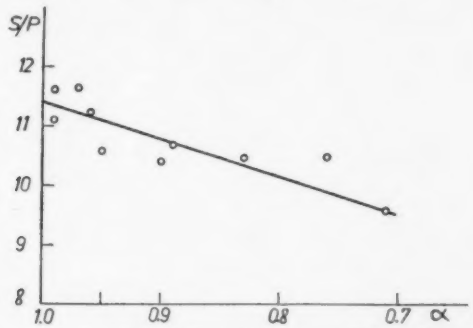

FIG. 5.—The function S/p vs. αH_0 for HCl.

Equation (12) indicates that S/p will be a straight line when plotted versus α. Using the α-values in Table 3, S/p from reference 24 is plotted against α in Fig. 5. As can be seen, it is possible to draw a straight line through the data giving

$$S_1 = 11{\cdot}4 \quad \text{and} \quad S_2 = 5{\cdot}3 \tag{15 a, b}$$

The agreement between $S_2 = 5{\cdot}3$ for HCl and $S_2 = 5{\cdot}32$ for $HClO_4$[24] is interesting but must be considered as fortuitous in view of the large spread of the data. It is worth emphasizing that combination of accurate H_0 and NMR measurements might provide a route for finding the dissociation of the hydrogen halides.

For the time being we shall consider the α-values in Tables 3 and 4 as the best at present available, and proceed to compute Ky_{HA} from (7) in an attempt to obtain values for the dissociation constants with the aid of the activities in HCl and HBr solutions discussed in reference 4. In Fig. 6 log Ky_{HA} is plotted against C for HCl, HBr, HNO_3 and $HClO_4$. The Ky_{HA}-values for HNO_3 and $HClO_4$ are those of reference 4. The currently accepted K-values for HNO_3 (23·5)[1c] and $HClO_4$ (38)[24] are also shown. Analogous extrapolations can be performed for HCl and HBr, but they must be considered as highly uncertain. In fact, the curve for $HClO_4$ in Fig. 6 can be fitted by the following three functions using least square procedures:

$$\log Ky_{HClO_4} = 1{\cdot}58 + 0{\cdot}224C + 0{\cdot}04321C^2 \tag{16a}$$

$$\log Ky_{HClO_4} = 0{\cdot}255 + 0{\cdot}564C + 0{\cdot}02237C^2 \tag{16b}$$

$$\log Ky_{HClO_4} = 0{\cdot}037 + 0{\cdot}7759C \tag{16c}$$

In (16a) the value for log $K = 1{\cdot}58$ given by REDLICH *et al.* was assumed to be known and the other two constants obtained by the method of least squares. The other two curves are first and second degree polynomials through the experimental points. The three expressions in (16) correspond to quite different K-values. This

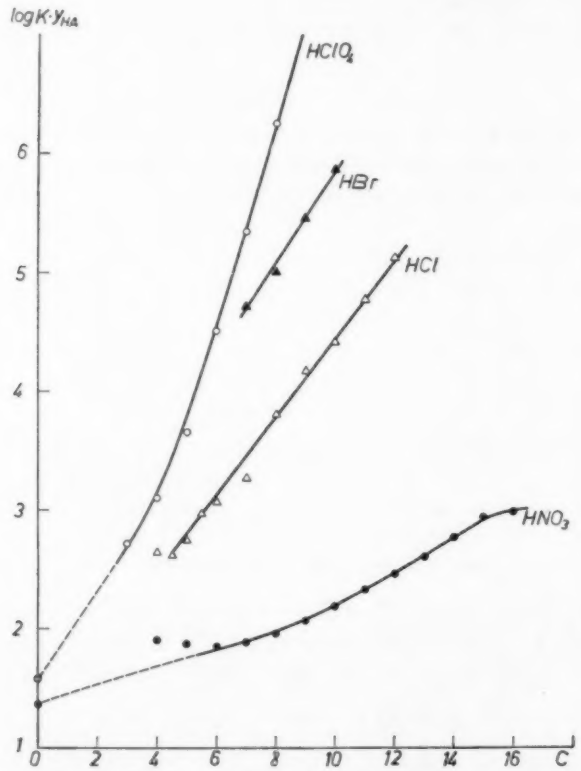

FIG. 6.—The function log Ky_{HA} vs. the stoicheiometric concentration of acid for: ● HNO_3 ○ $HClO_4$ △ HCl ▲ HBr.

uncertainty in the extrapolation procedure should also apply to HCl and HBr. At present only upper and lower limits can be assigned to their K-values by the following argument. As can be seen from Fig. 6, log Ky_{HA} is a linear function of C for HCl and HBr and the line has a slope of ~0·35. Such a high value for the salting-out constant of an uncharged molecule seems rather unusual. It is more likely that the curve will bend towards the ordinate as suggested in the extrapolation for $HClO_4$ by REDLICH *et al.* For HCl and HBr a lower limit can thus be obtained by a straight line extrapolation of the experimental data. It also seems highly unlikely that y_{HA} should pass through a minimum somewhere below the range of measurable concentrations, and the lowest experimental values for Ky_{HA} can thus be supposed to give an upper limit for K. In this way we find

$$1{\cdot}05 \leq \log K_{HCl} \leq 2{\cdot}60;\ 2{\cdot}15 \leq \log K_{HBr} \leq 4{\cdot}65 \qquad (17a, b)$$

The dissociation of the hydrogen halides has recently been discussed by BELL[25] with reference to the pertinent literature. Application of Raoult's law to HCl, HBr and HI has given the following K-values:[25]

$$\log K_{HCl} = 6; \qquad \log K_{HBr} = 8; \qquad \log K_{HI} = 9 \qquad (18a, c)$$

The discrepancy between the values in (17) and (18) amounts roughly to 10^4. The main reason may be, as indicated by Fig. 6, that Raoult's law cannot be used for estimating the concentration of undissociated acid. The application of Raoult's law in this instance requires that y_{HA} should be practically constant. In fact, y_{HA} varies considerably for all acids, from about one to two powers of ten for HNO_3 up to about six for $HClO_4$ and analogously for HCl and HBr. In view of this behaviour of y_{HA}, the K-values in (18) cannot be regarded as final. However, recently announced discrepancies between Raman and NMR measurements in $HClO_4$[26] indicate the possibility of a higher degree of dissociation than that obtained from the NMR-values used when evaluating the φy_{H^+}-values in Table 1. If these Raman data are correct the values for $HClO_4$ would shift towards the right in Fig. 1 in better agreement with the other acids. This would increase α and thus also the K-values for HCl and HBr.

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DISCUSSION

The method of estimating the hydrogen ion concentration from H_0 data seems to offer an alternative to other more elaborate methods such as the Raman and NMR methods. As may be seen from Table 2 it is also useful in dilute solutions, but here the emf and conductance methods are superior in accuracy. However, the simple experimental technique involved in measuring H_0 makes it attractive. It should also, be possible to improve the accuracy of the spectrophotometric technique to make it comparable with the other methods. This is especially important when it comes to the determination of α in HCl and HBr where these fail. Future measurements should also test the validity of the assumption of φy_{H^+} being the same function of H_0 for all strong acids.

Acknowledgements—The author is grateful to Professor L. G. SILLÉN for some valuable discussions and to the Swedish Atomic Energy Committee for financial support. Dr. V. TYRRELL corrected the English text.

[25] R. P. BELL, *The Proton in Chemistry*, Chap. VII. Cornell University Press, New York (1959).
[26] G. C. HOOD and C. A. REILLY, *J. Chem. Phys.* **32**, 127 (1960).

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CALCULATION OF THE COMPOSITION AND STABILITY OF SILVER AMMINE COMPLEXES FROM SOLUBILITY DATA

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(*Received* 26 *April* 1960)

Abstract—From a consideration of the data available in the literature on the solubility of silver chloride, silver bromide and silver thiocyanate in aqueous ammonia it is concluded that the principal complex ion formed is $[Ag(NH_3)_2]^+$. The stability has been calculated and the value of log β_2 found to be 7·3 at 25° and 7·0 at 15°.

IN previous publications DEY *et al.* [1-13] derived simple expressions enabling the direct calculation of the composition and stability of complexes in aqueous solution from solubility data. No account was taken of changes in activity factors, and it has now been thought necessary to pursue a more rigorous treatment to obtain more accurate values of the stability constants.

This paper records the recalculation of the results in a system of the type:

$$AgX + n\,NH_3 \rightleftharpoons [Ag(NH_3)_n]^+ + X^-$$

where X = Cl, Br or CNS. In our earlier calculations [5,7,12] the effect of X^- was omitted, and the effect of changes in activity factors was neglected.

In the above equilibrium, we may write:

$$\beta_n = [Ag(NH_3)_n{}^+][Ag^+]^{-1}[NH_3]^{-n};\quad K_s = [Ag^+][X^-]$$

From mass balance considerations also, we have:

$$s = [Ag(NH_3)_n{}^+] = [X^-];\quad c = [NH_3] + n[Ag(NH_3)_n{}^+]$$

where s is the concentration of AgX dissolved in aqueous ammonia of concentration c. By rearrangement we obtain:

$$s^2 = (c - sn)^n \beta_n K_s \qquad \text{(i)}$$

[1] A. K. DEY, *Dokl. Akad. Nauk SSSR* **50**, 1047 (1947).
[2] A. K. DEY, *Proc. Natl. Acad. Sci. India* **25** A, 202 (1956).
[3] A. K. DEY, *J. Indian Chem. Soc.* **24**, 207 (1947).
[4] A. K. DEY, *Proc. Natl. Acad. Sci. India* **25** A, 202 (1956).
[5] A. K. DEY, *Proc. Natl. Acad. Sci. India* **25** A, 205 (1956).
[6] R. L. SETH and A. K. DEY, *Proc. Natl. Acad. Sci. India*, **26** A, 312 (1957).
[7] A. K. DEY, *J. Inorg. Nucl. Chem.* **6**, 71 (1958).
[8] R. L. SETH and A. K. DEY, *Curr. Sci., India* **27**, 244 (1958).
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[10] R. L. SETH and A. K. DEY, *Z. Phys. Chem.* **210**, 108 (1959).
[11] A. K. DEY, K. C. MATHUR and R. L. SETH, *Proc. XVII Int. Cong. Pure & Appl. Chem. Munich*, Paper No. A 1076 (1959)
[12] K. C. MATHUR and A. K. DEY, *Proc. Symp. Chem. Co-ord. Compounds, Agra* 1959, **3**, 178 (1960).
[13] S. N. SINHA and A. K. DEY, *Vijñana Pari. Anu. Patrika* **2**, 111 (1959).
[13] A. K. DEY and R. L. SETH, *Proc. Symp. Chem. Co-ord. Compounds, Agra* 1959 **2**, 190 (1960).

and for other corresponding concentrations s' and c' we have

$$s'^2 = (c' - s'n)^n \beta_n K_s$$

Therefore,

$$\frac{s^2}{s'^2} = \left(\frac{c - sn}{c' - s'n}\right)^n$$

Taking logarithms of both sides, we have,

$$2 \log s/s' = n[\log (c - sn) - \log (c' - s'n)]$$

Expanding the right hand side as a power series and neglecting the second and higher terms (since s is small in comparison with c) we obtain:

$$n = \frac{2 \log s/s'}{\log c/c'} \qquad \text{(ii)}$$

From equation (i), we have

$$2 \log s = n \log (c - sn) + \log K_s \cdot \beta_n \approx n \log c + \log K_s \cdot \beta_n$$

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Thus from equation (ii) it is possible to calculate the value of n. The value can also be calculated from the slope of the curve relating log s and log c, the slope being equal to $n/2$. We have calculated the value of n in the systems investigated by both the methods.

In calculating the value of $K_s \cdot \beta_n$ corrections for the activities may be applied, using the approximation $-\log f_i = 0{\cdot}5\sqrt{I}(1 + \sqrt{I})^{-1}$, where f_i is the activity coefficient and the ionic strength $I = s$.

As will be seen from the table below, n has the value 2, and therefore

$$K_s \cdot \beta_2 = \frac{s^2 f_i^2}{(c - 2s)^2}$$

Individual values of n show some deviations from 2, but from the graph (Fig. 1) it may be seen that the value of n approximates closely to 2. Log $K_{s\,AgCl} = -9{\cdot}8$ at 25°[14], and hence log $\beta_2 = 7{\cdot}3$ at 25°.

TABLE 1.—THE SYSTEM AgCl–NH_3–H_2O at 25°[15]

Concn. of NH_3 (mM/l.)	AgCl dissolved (mM/l.)	n	log $K_s \cdot \beta_n$ ($n = 2$)
0·0288	0·00149	—	−2·50
0·0590	0·00304	2·5	−2·54
0·2530	0·01400	1·9	−2·52
0·3970	0·02270	2·1	−2·51
0·4280	0·02490	2·4	−2·50
0·8180	0·05140	2·2	−2·47
0·8630	0·05410	1·9	−2·48
0·9090	0·05840	2·8	−2·46
0·9610	0·06160	1·9	−2·46
1·9910	0·14700	2·4	−2·41

Average value of log $K_s \cdot \beta_n = -2{\cdot}5$

[14] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLEN, *Stability Constants* Part II. Chemical Society, London (1958).

[15] W. G. WHITNEY and A. C. MELCHER, *J. Amer. Chem. Soc.* **23**, 78 (1903).

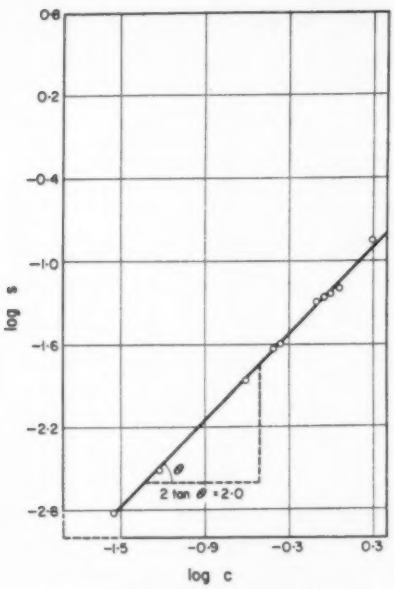

FIG. 1.—System $AgCl–NH_3–H_2O$ at 25° log c versus log s

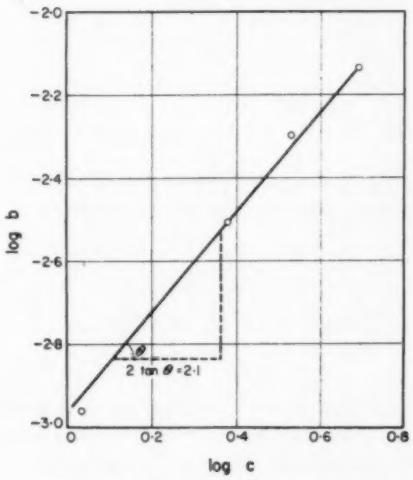

FIG. 2.—System $AgBr–NH_3–H_2O$ at 15° log c versus log s

TABLE 2.—THE SYSTEM $AgBr–NH_3–H_2O$ AT 15°[16]

Concn. of NH_3 (mM/l.)	AgBr dissolved (mM/l.)	n	log $K_s \cdot \beta_n$ ($n = 2$)
1·085	0·0011	—	−6·01
2·3650	0·0031	2·6	−5·81
3·410	0·0050	2·6	−5·73
4·950	0·0074	2·4	−5·72

Average value of log $K_s \cdot \beta_n = -5·8$

The value of n from (Fig. 2) approximates to 2. The value of log $K_{s_{AgBr}} = -12·8$ at 15°[14] and hence log $\beta_2 = 7·0$ at 15°.

TABLE 3.—THE SYSTEM $AgBr–NH_3–H_2O$ AT 25°[16]

Concn. of NH_3 (mM/l.)	AgBr dissolved (mM/l.)	n	log $K_s \cdot \beta_n$ ($n = 2$)
0·1932	0·0006	—	−5·03
0·3949	0·0012	2·0	−5·06
0·7573	0·0022	2·0	−5·11
1·9650	0·0069	2·3	−4·98
3·0240	0·0116	2·4	−4·92
5·2440	0·0244	2·6	−4·79

Average value of log $K_s \cdot \beta_n = -5·0$

[16] G. BÖDLANDER *Z. Phys. Chem.* **9**, 734 (1892). G. BÖDLANDER and R. FITTIG, *Z. Phys. Chem.* **39**, 597 (1901–02).

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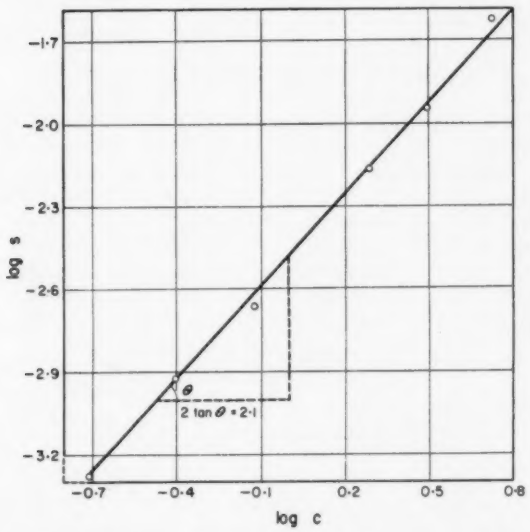

FIG. 3.—System $AgBr–NH_3–H_2O$ at 25° log c versus log s

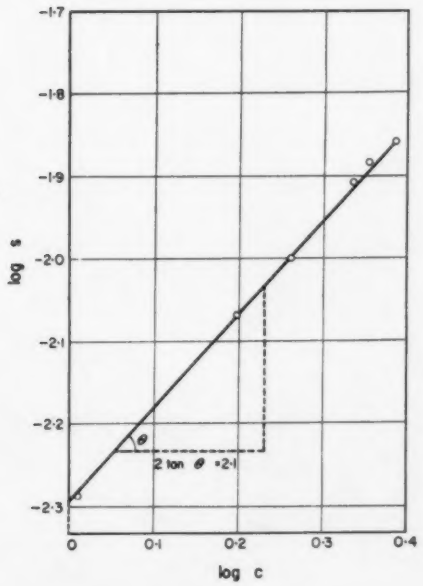

FIG. 4.—System $AgCNS–NH_3–H_2O$ at 25° log c versus log s

The value of n from Fig. 3 is approximately two. Log $K_{s_{AgBr}}$ at 25° is $-12{\cdot}2$[14], and hence log $\beta_2 = 7{\cdot}2$ at 25°.

The value of n from Fig. 4 is approximately 2. Log $K_{s_{AgCNS}}$ at 25° is $-11{\cdot}9$[14], and hence the value of log $\beta_2 = 7{\cdot}3$ at 25°.

TABLE 4.—THE SYSTEM AgCNS–NH_3–H_2O AT 25°[17]

Concn. of NH_3 (mM/l.)	AgCNS dissolved (mM/l.)	n	log $K_s \cdot \beta_n$ ($n = 2$)
1·026	0·00517	—	−4·65
1·587	0·00854	2·2	−4·61
1·840	0·01001	2·0	−4·61
2·178	0·01234	2·0	−4·58
2·276	0·01292	1·9	−4·58
2·440	0·01376	1·9	−4·59

Average value of log $K_s \cdot \beta_n = -4{\cdot}60$

The average value of log β_2 for the three systems at 25° is 7·3. At 15° log β_2 is found to be 7·0.

Acknowledgements—The authors are grateful to Professor LARS GUNNAR SILLÉN for helpful discussions during the visit of the senior author (A. K. D.) to the Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden. They are also thankful to the Council of Scientific and Industrial Research, India, for supporting the work and for the grant of a Fellowship to one of them (R. L. S.).

[17] F. J. GARRICK and C. L. WILSON, *J. Chem. Soc.* 835 (1932).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 317 to 324. Pergamon Press Ltd. Printed in Northern Ireland

THE RATES OF THE ELECTRON EXCHANGE REACTION BETWEEN U(IV) AND U(VI) IONS IN WATER, ETHYLENE GLYCOL AND WATER–ETHYLENE GLYCOL SOLVENTS

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(*Received* 13 *June* 1960; *in revised form* 4 *August* 1960)

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Abstract—The rate of the electron exchange reaction between U(IV) and U(VI) ions was studied at 25° in water, glycol and water–glycol solvents, and at various concentrations of U(IV), U(VI), and hydrochloric acid. The order of the reaction with respect to each of these substances was found to depend on the composition of the solvent. The rates of the reaction in the water–glycol were slower by factors of from two to about four orders of magnitude than were the rates of the reaction in the water–ethanol and water–acetone system. This slowing down of the reaction in water–ethylene glycol as compared to water–ethanol and water–acetone is attributed to the replacement of water in the inner solvation layer of the uranyl ion by the ethylene glycol.

THE rates and orders of the electron exchange reaction between U(IV) and U(VI) ions in the presence of hydrochloric acid have been studied in the water–ethanol and the water–acetone systems.[1,2,3] The rates and the orders of the reaction in each solvent system were found to depend on the composition of the solvent. But the dependences of the rates and the orders on solvent composition was different in the two solvent systems. Except for 30 per cent by volume organic-component of the solvent, the reaction rate was greater in ethanol–water solvent than in the glycol–water solvent. The dependence on solvent composition of the order of the reaction with respect to hydrochloric acid was entirely different in the solvent systems. The orders of the reaction with respect to U(IV) and U(VI) in the two solvent systems were somewhat similar, but the changes in order were more marked in the water–ethanol system. The data in water–acetone extended to only 90 volume per cent acetone and hence it was not possible to know whether the drastic changes in orders with respect to U(IV) and U(VI) occurred in the last 10 volume per cent change in solvent as were observed in the case of ethanol–water. Acetone as a solvent component had certain limitations that prevented the investigation in pure acetone.

It was thought to be of interest to study the reaction in glycol–water systems since the full solvent range could be investigated, and the effect of the last 10 per cent change in solvent ascertained. Also the comparison, with respect to their effect on the electron exchange reaction, of hydroxyl- and carbonyl-type solvents, it was felt, could better be made after a more extensive selection of solvents had been used. The glycol would have the further interest of being a dihydroxy-type solvent, which, because of

[1] D. M. MATHEWS, J. D. HEFLEY and E. S. AMIS, *J. Phys. Chem.* **63**, 1236 (1959).
[2] A. INDELLI and E. S. AMIS, *J. Amer. Chem. Soc.* **81**, 4180 (1959).
[3] S. L. MELTON, A. INDELLI and E. S. AMIS. *J. Inorg. Nucl. Chem.* in press.

chelation effect, would form more stable compounds with heavy metal ions than would monohydric alcohol, ethanol.[4]

EXPERIMENTAL

Experimental techniques, and the preparation and analysis of the solid UCl_4 and $UO_2 \cdot Cl_2 \cdot H_2O$ were as described by MATHEWS *et al.*[1]

The ethylene glycol used was Fischer certified reagent. It was not purified further.

Stock solutions and tracer solution were the same as described by MATHEWS *et al.*[1] The runs were made, sampled, and analysed as described by these authors except that ethylene glycol was substituted for ethyl alcohol in the present experiments.

TREATMENT OF DATA

The electron exchange rate was calculated using the equation

$$R = \frac{0{\cdot}693}{t_{\frac{1}{2}}} \cdot \frac{ab}{a+b} \qquad (1)$$

where a and b are the concentrations of U(IV) and U(VI) in the reaction vessel. R is the total number of exchanges, labelled and unlabelled, per unit time in the concentration units used.

The half-life, $t_{\frac{1}{2}}$, was obtained and R calculated from $t_{\frac{1}{2}}$, a and b in the manner previously described.[1] Plots of counts per minute vs. time from which the half-lives were determined showed our precision to be 10 per cent or better. Our care in weighing, volume measurements, counting, and analytical procedures were such that we feel our accuracy was well within the limits of our precision.

Fig. 1 shows the plots of $-\log R$ corrected for constant concentrations and orders vs. $-\log C$ which were used to determine the order of the reaction with respect to U(IV). Each line has a slope which is the order of the reaction with respect to U(IV) at the solvent composition specified. The precision of the data is indicated by the fit of the data points to the lines. The line for the pure water points from the data of RONA[5] is included in the drawing for reference purposes. The orders of the reaction with respect to U(VI) and hydrochloric acid were determined in a similar manner, and the data for these plots show the same consistency as the data for U(IV) in Fig. 1.

The data for Fig. 1 were obtained by making, for each solvent composition, several different runs with the same initial concentrations of U(VI) and of hydrochloric acid but different initial concentrations of U(IV). The initial rates were determined, and the logarithms of these rates plotted against the logarithms of the initial concentrations of U(IV). This gave the order of the reaction with respect to U(IV). In like manner the orders with respect to U(VI) and hydrochloric acid were found. Then to check the reliabilities of the orders so determined, all pertinent data were included on the plots by introducing the concentrations of the reactants raised to the powers represented by their respective orders. This procedure was followed in all the order plots for the various reactants. This procedure did not change the slopes of the lines and thus confirmed the orders. The intercepts of the lines were of course changed.

The half-lives, rates, and specific velocity constants at 25°C for the U(IV)–U(VI) electron exchange reaction is given in Table 1.

[4] J. C. BAILAR (Editor) *Chemistry of the Co-ordination Compounds*, p. 24. Reinhold, New York (1956).
[5] E. RONA, *J. Amer. Chem. Soc.* **72**, 4339 (1950).

TABLE 1.—HALF-LIVES, RATES AND SPECIFIC VELOCITY CONSTANTS AT 25·00°C FOR THE U(IV)–U(VI) ELECTRON EXCHANGE REACTION

U(IV)	U(VI)	[H⁺]	$t_{\frac{1}{2}}$ (hr)	$R \times 10^7$ (mole/l/min)	$k' \times 10^4$
		30% Ethylene glycol			
0·03751	0·01079	0·1216	72	13·4	0·195
0·03751	0·01079	0·2148	165	5·892	0·185
0·03751	0·01079	0·3544	279	3·485	0·216
0·01896	0·01344	0·1322	91·5	9·916	0·232
0·01896	0·02333	0·1323	83	14·56	0·234
0·01896	0·03323	0·1324	74	18·84	0·239
0·00938	0·01167	0·1654	175	3·431	0·202
0·03792	0·01699	0·1799	102	13·24	0·239
		60% Ethylene glycol			
0·01875	0·01034	0·2619	290	2·654	1·67
0·01875	0·01034	0·1957	195	3·942	1·60
0·01875	0·01034	0·3354	382	2·015	1·62
0·00938	0·01012	0·1993	372	1·510	1·25
0·02813	0·01057	0·2105	216	4·109	1·27
0·03751	0·01079	0·2148	187	5·176	1·27
0·01875	0·01034	0·1173	118	6·538	1·61
0·01875	0·01034	0·1320	148	5·200	1·47
0·01875	0·01034	0·1516	146	5·270	1·65
0·01875	0·01034	0·1122	138	5·593	1·36
0·01875	0·02024	0·1123	104	10·81	1·39
0·01875	0·03013	0·1124	80	16·69	1·47
		90% Ethylene glycol			
0·01806	0·00720	0·1269	78	7·619	139
0·01806	0·00720	0·1858	70	8·488	141
0·01806	0·00720	0·2646	64	9·285	142
0·01806	0·01395	0·1858	70	12·99	128
0·01806	0·02070	0·1858	60	18·57	134
0·01806	0·02746	0·1858	54	23·30	135
0·00902	0·00698	0·1965	147	3·090	133
0·02708	0·00742	0·2114	49	13·73	128
0·03612	0·00764	0·2189	31·5	23·12	139
		100% Ethylene glycol			
0·01815	0·00723	0·1904	78	7·657	3·19
0·01815	0·00723	0·2694	94	6·356	3·18
0·01815	0·00723	0·1272	63	9·480	3·19
0·01815	0·01402	0·1272	57	16·02	2·85
0·01815	0·02081	0·1272	48	23·32	2·96
0·00907	0·00698	0·1215	75	6·079	3·02
0·02722	0·00742	0·1362	54	12·48	3·02
0·03630	0·00765	0·1436	50	14·59	2·97

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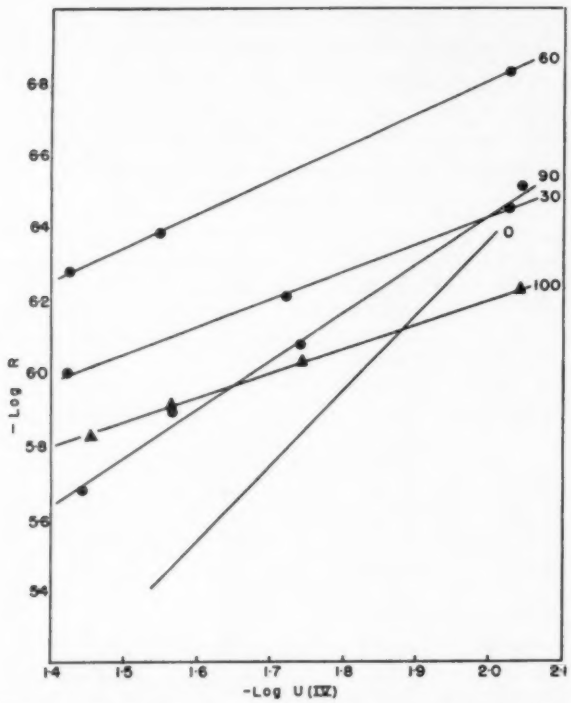

FIG. 1.—A plot of $-\log R$ against $-\log C$ of U(IV) at constant concentrations of U(VI) and H^+ and for various compositions of the solvent. The numbers on the various curves indicate the volume per cent of ethylene glycol.

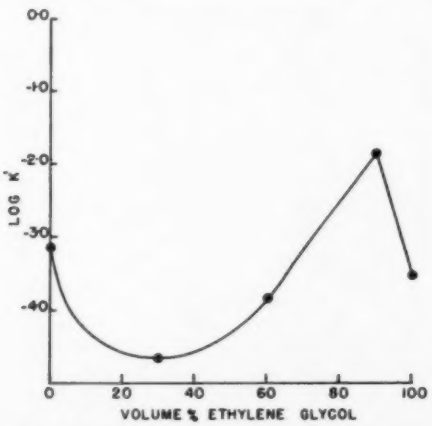

FIG. 2.—Logarithm of the specific velocity constant vs. the volume per cent ethylene glycol in the solvent.

In Fig. 2 the logarithm of the averages of the specific velocity constants are plotted as ordinate against the volume per cent ethylene glycol in the solvent. The objections to such a plot and the advantages which out-weigh the objections have been discussed.[3] The dependence of the specific velocity constant on solvent composition in

water–glycol solvent is quite different from this dependence in either water–ethanol or water–acetone solvent systems. Neither of these last two solvent systems show an initial decrease in log k with volume per cent organic component of the solvent. Both of these solvent systems do show maxima in the plots, and the maximum in the case of the water–ethanol system occurs in approximately the same region of composition with respect to organic component of solvent as does the maximum in the case of the water–glycol solvent.

TABLE 2.—ORDERS OF THE U(IV)–U(VI) ELECTRON EXCHANGE REACTION WITH RESPECT TO THE VARIOUS REACTANTS IN DIFFERENT SOLVENTS

Volume per cent ethylene glycol	U(IV) Order	U(VI) Order	[H+] Order
0	2·0	1·0	−3·0
30	0·75	0·68	−1·35
60	0·95	0·91	−1·14
90	1·35	0·79	0·24
100	0·66	0·85	−0·53

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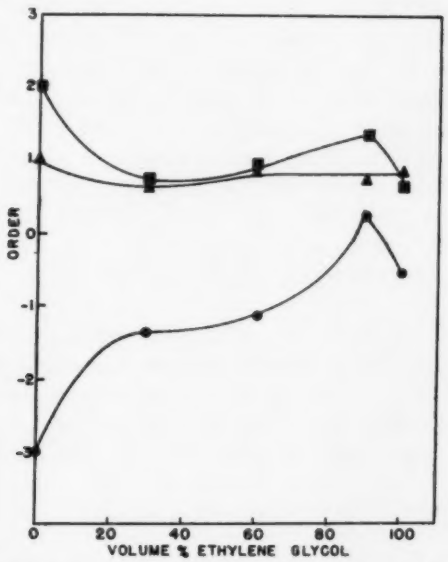

FIG. 3.—Order of the various reactants versus the volume per cent ethylene glycol: ●, acid; ▲, U(VI): ■, U(IV).

In Table 2 are presented the orders with respect to various reactants of the U(IV)–U(VI) electron exchange reaction in solvents of different compositions. The graphical representation of these data are shown in Fig. 3.

The curve for the order of the reaction with respect to U(IV) in the water–glycol system has the general shape of the curve for the order of the reaction with respect to U(IV) in water–ethanol. Both curves show a decrease to a minimum of the order with respect to U(IV) as the solvent becomes richer in the organic component of the solvent.

The minimum occurs at a composition of solvent somewhat richer in the organic component in the water–ethanol system. Both curves reach a maximum at 90 volume per cent of the organic component, but the maximum is over twice as great in the water–ethanol compared to the water–glycol. Both curves then show a precipitous decrease from 90 volume per cent to 100 volume per cent organic component of the solvents. The decrease is to zero and 0·66 volume per cent in the water–ethanol and water–glycol solvents, respectively. The curve for the order with respect to U(IV) in the water–acetone solvent had the same general shape as for the solvents discussed above, except that the data only extended to 90 volume per cent acetone.

The order with respect to U(VI) first decreases slightly with increasing volume per cent glycol and then shows a gradual increase out to 100 volume per cent glycol. There is not the sudden decrease from about 60 out to 90 volume per cent organic component of the solvent as found in water–ethanol and in water–acetone, and then the still more rapid increase out to 100 volume per cent as found in water–ethanol.

Except for the initial increase in order with respect to hydrochloric acid out to 30 volume per cent organic component of the solvent in the three solvent systems, the curves of order versus volume per cent organic component of the solvent have no other similarities in the three solvent systems.

The complex ions and kinetic expressions proposed by MATHEWS, *et al.*[1] will, under certain limiting conditions, account fairly well for the observed orders out to 90 volume per cent glycol; 30 volume per cent showing the greatest deviation.

The most interesting observation is that the order is positive with respect to hydrochloric acid in 90 volume per cent glycol. MELTON *et al.*[3] observed a positive order with respect to hydrochloric acid in water–acetone when the hydrochloric acid was less than 0·1 M. But in the present data in water–glycol, the order with respect to hydrochloric acid is +0·24 even when the acid is 0·2646 molar. In this discussion order with respect to H^+ is used as identical with order with respect to hydrochloric acid since the activity of hydrogen ion in solvents containing glycol are not readily ascertained.

SULLIVAN *et al.*[6] in the Np(V)–Np(VI) electron exchange reaction found that a path involving hydrogen ion presumably becomes increasingly important. They observed that the rate increased linearly with hydrogen ion concentration in the range of hydrogen ion concentration from 0·1 to 3·0 mole/l. They suggest the acid reaction path involves specific hydronium ion catalysis and give the mechanism as a two step process

$$Np^*O_2^+ + H^+ \rightleftarrows Np^*O_2H^{2+}$$

and

$$NpO_2^{2+} + Np^*O_2H^{2+} \rightleftarrows [X^{4+}]^\ddagger \rightarrow Np^*O_2^{2+} + NpO_2H^{2+}.$$

DUKE and PINKERTON[7] give a mechanism for the U(V) disproportionation which involves the transfer of a hydroxyl group. Thus:

$$UO_2^+ + H^+ \rightleftarrows UO_2H^{2+}$$

$$O\text{–}U\text{–}OH^{2+} + O\text{–}U\text{–}O^+ \rightleftarrows [X^{3+}]^\ddagger \rightarrow O\text{–}U^{2+} + HO\text{–}U\text{–}O_2^+.$$

HARKNESS and HALPERN[8] attribute the non-integral inverse order, ranging from

[6] J. C. SULLIVAN, D. COHEN and J. C. HINDMAN, *J. Amer. Chem. Soc.* **79**, 3672 (1957).
[7] F. R. DUKE and R. C. PINKERTON, *J. Amer. Chem. Soc.* **73**, 2361 (1951).
[8] A. C. HARKNESS and J. HALPERN, *J. Amer. Chem. Soc.* **81**, 3526 (1959).

−1·48 at 16° to −1·39 at 25°, with respect to hydrogen ion of the U(IV)–Tl(III) reaction to be due to simultaneous contributions from two separate paths inversely first- and second-order, respectively, in H^+.

Suppose that inversely first- and second-order reactions with respect to hydrochloric acid are operative simultaneously with a direct second-order reaction with respect to hydrochloric acid in the present reaction in 90 volume per cent ethylene glycol. The resulting over-all order of the reaction could be +0·24 with respect to

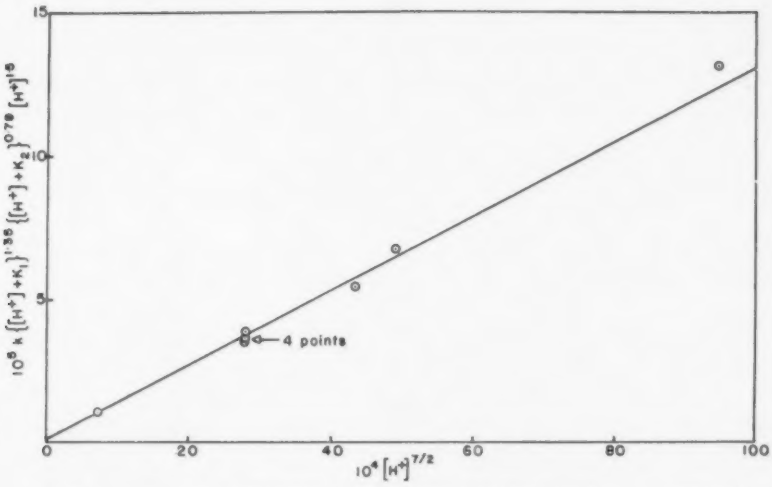

FIG. 4.—A plot of $10^5 k\{[H^+] + K_1\}^{1.35}\{[H^+] + K_2\}^{0.79}[H^+]^{1.5}$ versus $10^4[H^+]^{7/2}$

hydrochloric acid, represented here as H^+, according to the following rate equation for the rate R,

$$R = [UOH^{3+}]^{1.35}[UO_2H^+]^{0.79}\{k_1[H^+]^{-1.5} + k_2[H^+]^2\} \tag{2}$$

Substituting the value for $[UOH^{3+}]$ and $[UO_2H^+]$ in terms of [U(IV)] and [U(VI)] as given by MATHEWS *et al.*[1] the rate expression becomes

$$R = \left\{\frac{K_1[U(IV)]}{([H^+] + K_1)}\right\}^{1.35}\left\{\frac{K_2[U(VI)]}{([H^+] + K_2)}\right\}^{0.79}(k_1[H^+]^{-1.5} + k_2[H^+]^2) \tag{3}$$

The specific velocity constant k' is found by dividing the rate by $[U(IV)]^{1.35}[U(VI)]^{0.79}$ and is

$$k' = \left\{\frac{K_1}{([H^+] + K_1)}\right\}^{1.35}\left\{\frac{K_2}{([H^+] + K_2)}\right\}^{0.79}(k_1[H^+]^{-1.5} + k_2[H^+]^2) \tag{4}$$

This can be put in the form

$$k\{[H^+] + K_1\}^{1.35}\{[H^+] + K_2\}^{0.79}[H^+]^{1.5} = k_1 + k_2[H^+]^{3.5} \tag{5}$$

where k is the observed specific velocity constant. The left hand side of the equation plotted versus $[H^+]^{3.5}$ should be a straight line with the intercept equal to k_1 and the slope equal to k_2. The plot for such a calculation is given in Fig. 4 and is a straight line over a more than thirteen-fold range of $[H^+]^{3.5}$. The values of k_1 and k_2 from the

plot are $1{\cdot}0 \times 10^{-6}$ and $1{\cdot}3 \times 10^{-2}$. In these calculations K_1 and K_2 are assumed to be $3{\cdot}4 \times 10^{-2}$ and $1{\cdot}3 \times 10^{-5}$ as found in water.[1] The values of k_1 and k_2 inserted in equation (5) reproduce the data to within an average of 3·5 per cent with the maximum deviation between observed and calculated results being 6·0 per cent.

While as has been pointed out to the authors and as the authors realized, orders are many times reported to the nearest whole number, yet it seemed advisable to report the experimentally determined orders since in many cases the orders were so far removed from integral values. For example the orders for U(IV), U(VI) and $[H^+]$ in 30 volume per cent glycol are, respectively, 0·75, 0·68 and −1·35.

The mechanistic picture for the second order dependence of the U(IV)–U(VI) reaction on hydrochloric acid or, as used here, hydrogen ion can be expressed in the following manner:

$$U^*O_2^{2+}\cdot 6H_2O + 2H^+ \rightleftarrows U^*(OH)_2^{4+}\cdot 6H_2O$$

$$U^*(OH)_2^{4+}\cdot 6H_2O + U^{4+}\cdot 8H_2O \rightleftarrows [X^{+8}]^{\ddagger} \rightarrow U^{*4+}\cdot 8H_2O + U(OH)_2^{4+}\cdot 6H_2O.$$

This mechanism like that of SULLIVAN *et al.*[6] suggests a specific hydronium ion catalysis in the reaction path involving hydrochloric acid or hydrogen ion to a positive power.

Each solvent could be treated in detail, but the example given is illustrative of the necessary technique and the complexities involved. For example the −1·35 order with respect to hydrochloric acid in 30 volume per cent glycol can be interpreted fairly closely in terms of simultaneous contributions from two separate paths inversely first- and second-order, respectively, in hydrochloric acid. HARKNESS and HALPERN[8] used this method to explain a −1·39 order of the U(IV)–Tl(III) reaction with respect to hydrogen ion at 25°.

One can speculate that the slowing down of the electron-exchange-reaction by two to about four orders of magnitude in ethylene glycol-containing solvents as compared to solvents containing acetone or ethanol could arise from the chelation effects of the ethylene glycol, because of which the glycol would form stable compounds with heavy metal ions. Each glycol molecule would replace two waters of solvation in the inner solvation layer of the uranium ions, thus modifying the concentrations of water solvated and hydroxyl intermediates by influencing the equilibra involving water. Further the chelate ions while possibly able to exchange electrons would perhaps do so at a different velocity than would water-solvated and hydroxylated ions.

Acknowledgement—The authors are grateful to the United States Atomic Energy Commission for Contract AT-(40-1)-2069 which supported this research financially.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 325 to 333. Pergamon Press Ltd. Printed in Northern Ireland

THE RATES OF THE ELECTRON EXCHANGE REACTIONS BETWEEN U(IV) AND U(VI) IONS IN WATER AND WATER–ACETONE SOLVENTS

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(*Received* 13 *June* 1960; *in revised form* 4 *August* 1960)

Abstract—The rate of the electron exchange reaction between U(IV) and U(VI) ions was studied at 25° in water and water–acetone mixtures containing 30, 60, and 90 per cent by volume acetone, and at various concentrations of U(IV), U(VI), and hydrochloric acid. The order of the reaction with respect to each of these solutes was found to depend strongly upon the composition of the solvent. A departure in the trend of the rate dependence on hydrogen ion concentration was found for more dilute acid concentrations in sixty volume per cent acetone. Comparisons of the kinetics of the reaction in acetone–water and in ethanol–water are made. Mechanistic and kinetic discussions are included.

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MATHEWS *et al.*[1] studied the reaction between U(IV) and U(VI) ions in the presence of hydrochloric acid in water, ethanol, and water–ethanol solvents. These investigators found that the order of the reaction with respect to U(IV), U(VI), and hydrogen ions depended strongly upon the composition of the solvent in the water–ethanol system. INDELLI and AMIS[2] investigated the temperature coefficient of this reaction in this solvent system. The energy of activation was found to decrease with increasing weight per cent of alcohol in the solvent in general correspondence with an increase in reaction rate. No light or wall effects were found. RONA[3] studied the U(IV)–U(VI) reaction in water and found no salt effects.

It was felt by INDELLI and AMIS that the reaction should be studied in other solvent systems. The solvent system chosen in the present investigation was water–acetone since the dielectric constant range would be similar to that of the water–ethanol solvent system and, at the same time, acetone would contrast with alcohol in that the former has a carbonyl rather than a hydroxyl group.

EXPERIMENTAL

Solid UCl_4 and $UO_2Cl_2 \cdot H_2O$ were prepared as described elsewhere.[4] Experimental techniques, the preparation and analysis of stock solutions, and the tracer solution were as described by MATHEWS *et al.*[1]. The runs were made, sampled, and analysed as described by these except that acetone was substituted for ethyl alcohol in the present experiments, and hydrofluoric acid was used as the precipitating agent. Aliquots of the U(VI) solution (50 λ) were spotted on platinum disks, dried and counted. The U(IV) precipitate was dissolved in concentrated nitric acid, evaporated to dryness, taken up in 1 ml of dilute nitric acid, and a 50 λ portion spotted, dried and counted. Triplicate samples for each valence type were spotted, counted, and the average of these were used to obtain a point on the rate plot.

Fisher certified, A.C.S. grade acetone was used without further purification.

[1] D. M. MATHEWS, J. D. HEFLEY and E. S. AMIS, *J. Phys. Chem.* **63**, 1236 (1959).
[2] A. INDELLI and E. S. AMIS, *J. Amer. Chem. Soc.* **81**, 4180 (1959).
[3] E. RONA, *J. Amer. Chem. Soc.* **72**, 4339 (1950).
[4] D. M. MATHEWS, J. D. HEFLEY and E. S. AMIS, *J. Inorg. Nucl. Chem.* **12**, 84 (1959).

TREATMENT OF DATA

The electron exchange rates were calculated using the equation

$$R = \frac{0{\cdot}693}{t_{\frac{1}{2}}} \cdot \frac{ab}{a+b} \tag{1}$$

where a and b are concentrations of U(IV) and U(VI) in the system. R is the total

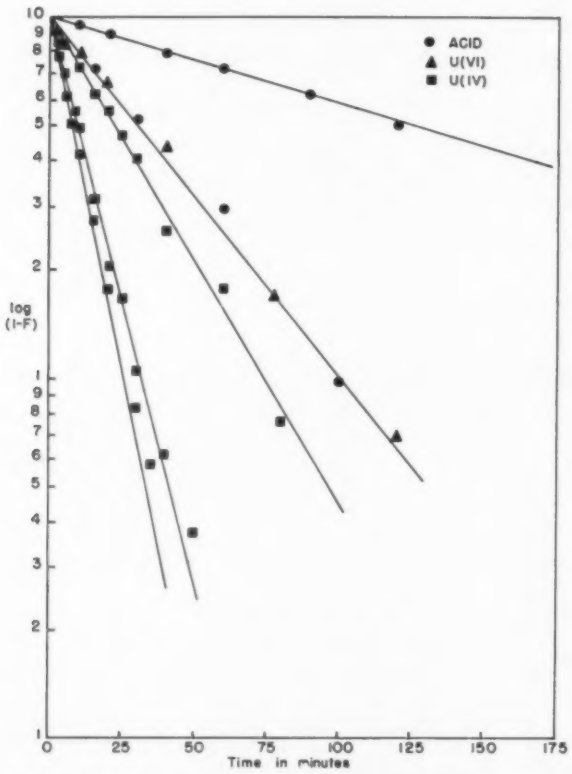

FIG. 1.—Logarithm $(1 - F)$ vs. time in minutes when the solvent was 30 per cent acetone.

number of exchanges, labelled and unlabelled, per unit time in the concentration units used.

The half-life, $t_{\frac{1}{2}}$, was obtained and R calculated from $t_{\frac{1}{2}}$, and a and b in the manner previously described.[1] The count-rate data was converted to 1-fraction (1-F) of complete exchange and a plot of such data for 30 weight per cent acetone is shown in Fig. 1. In this figure the solid circles represent data taken when the concentration of acid was varied and the concentrations of U(VI) and of U(IV) were held constant. The triangles represent data taken when the concentration of U(VI) was varied and the concentrations of acid and U(IV) were held constant. The squares represent data taken when the concentration of U(IV) was varied and the concentrations of the other substances were held constant. Initial concentrations are referred to here.

Figure 2 shows the plots of $-\log R$ corrected for constant concentrations and order

vs. $-\log C$ which were used to determine the order of the reaction with respect to U(IV); in Fig. 3 are given the plots of $\log R$ corrected for constant concentrations and orders versus $-\log C$ used to find the order of the reaction with respect to hydrogen ion. Each line has a slope which is the order of the reaction with respect to that reactant at the solvent composition specified. The line for pure water solvent from the data of RONA[3] was included in the drawings for reference purposes. The orders

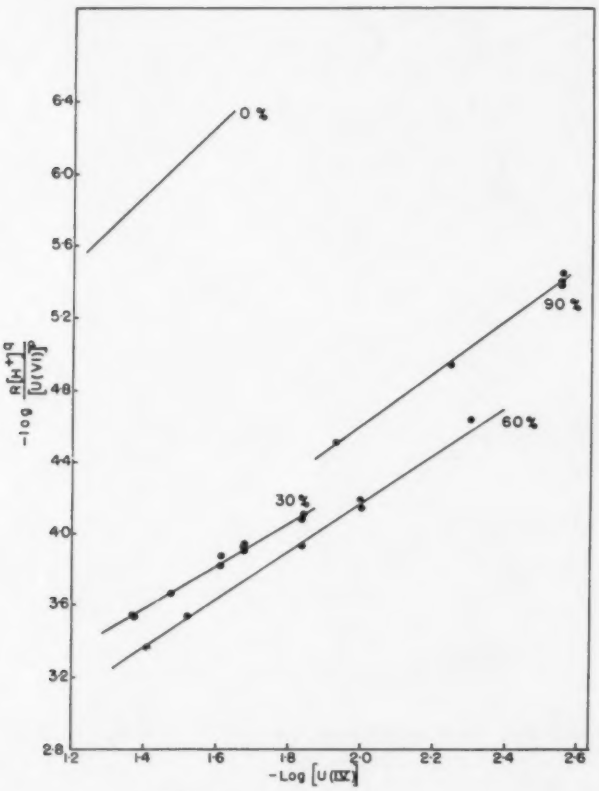

FIG. 2.—Plots of $-\log \frac{R[H^+]^q}{[U(VI)]^p}$ vs. $-\log$ [U(IV)] used in the determination of the order, r, of the reaction with respect to U(IV).

of the reaction with respect to U(VI) were determined in a similar manner and the data for these plots showed the same consistency as the data for U(IV) in Fig. 2.

The data for Fig. 2 were obtained by making, for each solvent composition, several different runs with the same initial concentrations of U(VI) and of H^+ but different initial concentrations of U(IV). The initial rates were determined, and the logarithms of these rates plotted against the logarithms of the initial concentrations of U(IV). This gave the order of the reaction with respect to U(IV). In like manner the orders with respect to U(VI) and H^+ were found. Then to prove the reliabilities of the orders so determined, all pertinent data were included on the plots by introducing the concentrations of the reactants raised to the powers represented by their

respective orders. This was likewise the procedure followed in arriving at Fig. 3. This procedure did not change the slopes of the lines and thus confirmed the orders. The intercepts of the lines were changed of course.

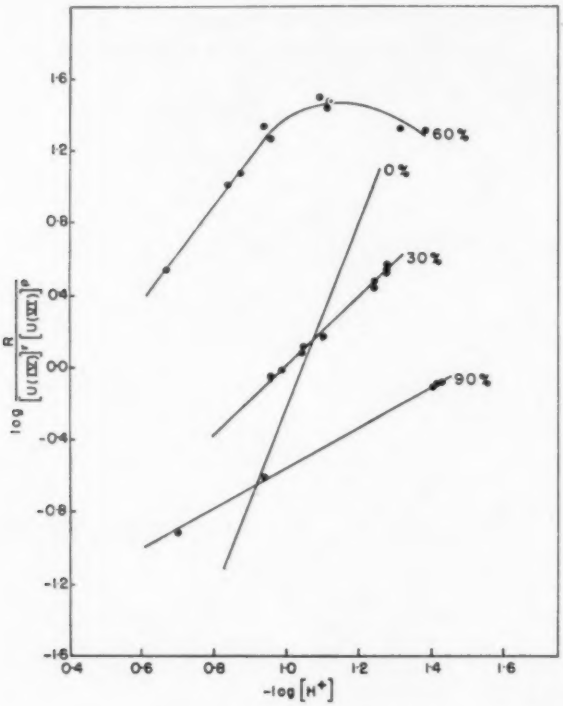

FIG. 3.—Plots of $\log \frac{R}{[U(IV)]^q[U(VI)]^p}$ vs. $-\log [H^+]$ used in the determination of the order, q, of the reaction with respect to H^+.

TABLE 1.—ORDERS OF THE VARIOUS REACTANTS IN THE DIFFERENT SOLVENTS

Acetone (%)	U(IV)	U(VI)	Hydrogen ion
0	2·0	1·0	−3·0
30	1·25	1·0	−1·85
60	1·33	1·13	−2·85 (above 0·1 M concentration)
90	1·47	0·59	−1·17

The orders of the reaction with respect to U(IV), U(VI) and hydrochloric acid are presented in Table 1 at various solvent compositions.

The orders for pure water solvent are those of RONA.[3] The orders in the other solvents were determined in this investigation. From Table 1 the orders are seen to have a marked dependence on the composition of the solvent.

Between zero and ninety volume per cent acetone, the order of the reaction with respect to U(IV) first decrease with added acetone and reaches a minimum at about

40 volume per cent acetone of about 1·22, then with further addition of acetone, the order with respect to U(IV) again increases and becomes about 1·50 at 90 volume per cent acetone which was as far as the data extend. The general shape of the curve is similar to that found by MATHEWS *et al.*[1] for the order with respect to U(IV) for the same reaction in ethanol–water solvents. In the latter case the minimum was lower by about 0·40 and was reached at about 50 volume per cent ethanol. Also in

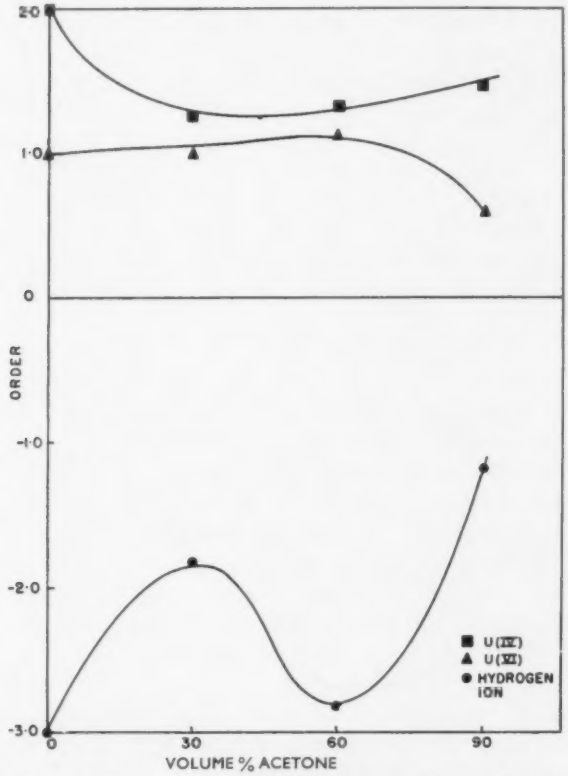

FIG. 4.—Orders of the various reactants vs. volume per cent ethanol.

the latter case the decrease in order was more gentle and the increase more abrupt with added alcohol, the value at 90 volume per cent alcohol being 2·89. Since the water–acetone data unfortunately extended only to 90 volume per cent, it was not possible to know whether there was the abrupt decrease in order with respect to U(IV) in pure acetone compared to the order in 90 volume per cent acetone as was found for pure ethanol compared to 90 volume per cent ethanol; (see Fig. 4.)

In the case of the order with respect to U(VI) the shape of the curve out to 90 volume per cent acetone closely resembles the curve found for the U(VI) order out to 90 volume per cent alcohol. In both cases there is first a slight increase in the order out to about 60 volume per cent organic component of the solvent and then a more precipitous decrease of the order out to 90 per cent by volume of the organic component. In the case of the water–acetone solvent the order dips to 0·59 at 90 volume per cent acetone while in the case of water–ethanol solvent the order drops to 0·10

at 90 volume per cent ethanol. In the case of acetone there is no way of knowing whether there is an abrupt rise of order beyond ninety volume per cent acetone as there was an abrupt rise of order beyond 90 volume per cent ethanol.

It might be mentioned the runs in 100 per cent acetone were not made since pure acetone at the acidity used in the runs polymerized rather rapidly. It was thought that this change in the nature of the solvent might affect the electron exchange reaction rate in a manner different from the other solvent factors. In water-diluted acetone, the polymerization was slower and the exchange reaction rate could be determined before extensive polymerization occurred.

It is the order of the reaction with respect to hydrogen ion in water–acetone which contrasts sharply with that in water–ethanol, especially at 60 volume per cent organic component of the solvent. In the case of water–ethanol the order with respect to hydrogen ion at first increases with increasing volume per cent ethanol, reaches a maximum at about 70 volume per cent and then decreases gradually out to 100 per cent ethanol. In the case of water–acetone solvent there is a maximum in the order with respect to hydrogen ion at about 30 volume per cent acetone, a minimum at about 60 volume per cent, and then an increase out to 90 volume per cent which is as far as the data go.

In addition to the minimum in the order with respect to hydrogen ion at 60 volume per cent acetone, there is also the curious hook in the log R vs. $-\log C$ curve for hydrochloric acid (Fig. 3) in this solvent. In Table 2 where half-lives, rates and specific velocity constants at various concentrations of reactants in various compositions of solvents are listed, it is to be noted that the specific velocity constants for these runs with the anomalous orders with respect to hydrogen ion are omitted. It will be noted that the hydrochloric acid concentrations in these anomalous runs were below 0·1 M in every case. At these low acid concentrations in 60 volume per cent acetone, the slope of the curve in Fig. 3 (right hand portion of 60 volume per cent curve) indicates a positive coefficient for the dependence of the rate upon hydrogen ion concentration. Since there was insufficient data in this region of acid concentration, the order with respect to hydrogen ion was not obtained and the specific velocity constants were therefore not calculated. Lower acid concentrations in this solvent would have been investigated except that the solutions proved unstable at lower acidities and hydrolysed complexes of uranium precipitated. As observed from Table 2 the order with respect to acid in each of the other solvents was consistently constant over the whole range of acid studied.

The rate expressions proposed by MATHEWS *et al.*[1] namely,

$$\frac{dx}{dt} = \frac{[U(IV)]^2[U(VI)]}{\left[\frac{[H^+]}{K_1} + 1\right]^2\left[\frac{[H^+]}{K_2} + 1\right]} \tag{2}$$

and

$$\frac{dx}{dt} = \frac{[U(IV)][U(VI)]}{\left[\frac{[H^+]}{K_1} + 1\right]\left[\frac{[H^+]}{K_2} + 1\right]} \tag{3}$$

to explain the observed orders found in the water–ethanol solvent up to 60 volume per cent of ethanol can be used in the present investigation to explain the observed

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TABLE 2.—RATES, CONCENTRATIONS OF EACH COMPONENT, HALF-LIVES AND SPECIFIC VELOCITY CONSTANTS AT 25·00°C FOR U(IV)–U(VI) EXCHANGE REACTION IN 30, 60 AND 90 PER CENT ACETONE

U(IV)	U(VI)	[H⁺]	$t_{\frac{1}{2}}$ (min)	$R \times 10^5$ (mole/l./min)	$k' \times 10^2$
		30% Acetone			
0·0213	0·0105	0·1027	57·75	8·44	1·440
0·0213	0·0105	0·0912	45·0	10·83	1·510
0·0427	0·0105	0·0912	23·0	25·39	1·484
0·0213	0·0105	0·0797	37·0	13·17	1·431
0·0339	0·00926	0·0528	11·25	44·80	1·441
0·0242	0·0185	0·0574	13·75	52·85	1·513
0·0242	0·0130	0·0574	17·5	33·49	1·365
0·0145	0·00926	0·0528	23·4	16·74	1·557
0·0436	0·00926	0·0528	8·4	63·02	1·480
0·0145	0·0130	0·0528	23·5	20·21	1·339
0·0145	0·00370	0·0528	31·5	6·48	1·509
0·0145	0·00370	0·1090	120·0	1·70	1·514
					Ave. 1·465
		60% Acetone			
0·01453	0·003704	0·1099	20·75	9·859	2·833
0·01453	0·003704	0·1342	32·5	6·295	3·196
0·01453	0·003704	0·1136	18·0	11·37	3·562
0·01453	0·003704	0·2121	107·0	1·912	3·579
0·01453	0·003704	0·1434	37·5	5·456	3·347
0·01453	0·003704	0·07859	12·5	16·36	—
0·01453	0·003704	0·04733	17·3	11·83	—
0·01453	0·003704	0·04037	17·0	12·04	—
0·01453	0·003704	0·07457	14·0	14·62	—
0·01453	0·003704	0·07457	13·5	15·15	—
0·02977	0·005434	0·1443	17·8	17·89	2·791
0·03970	0·005814	0·1468	13·2	26·62	2·755
0·004945	0·004484	0·1474	165·0	0·988	2·215
0·009889	0·004674	0·1488	72·0	3·055	2·671
0·009924	0·01376	0·1492	38·5	10·22	2·758
0·009924	0·008969	0·1492	60·0	5·44	2·284
					Ave. 2·908
		90% Acetone			
0·002808	0·0007191	0·1185	492	0·0806	2·680
0·002808	0·0007191	0·2015	885	0·0448	2·773
0·002808	0·0007191	0·03962	128	0·3099	2·858
0·002808	0·002549	0·03962	150	0·6172	2·698
0·002808	0·001938	0·03962	143	0·5556	2·855
0·01127	0·001046	0·03755	21·9	3·029	2·727
0·005636	0·000828	0·03892	52·0	0·9622	2·872
					Ave. 2·780

orders up to 30 volume per cent acetone. The equations, however, fail to show in 60 volume per cent acetone the order with respect to hydrogen ion is approximately negative three while the orders with respect to U(IV) and U(VI) remain nearly unity.

If we consider the equilibrium:

$$U^{4+} + 2H_2O \rightleftarrows U(OH)_2^{2+} + 2H^+$$

the equilibrium constant, K_3, is

$$K_3 = \frac{[U(OH)_2^{2+}][H^+]^2}{[U^{4+}]} \tag{4}$$

and the $U(OH)_2^{2+}$ concentration is given by the expression

$$[U(OH)_2^{2+}] = \frac{K_3}{[H^+]^2}([U(IV)] - [U(OH)_2^{2+}]) = \frac{K_3[U(IV)]}{[H^+]^2\left(1 + \frac{K_3}{[H^+]^2}\right)} \tag{5}$$

and we can explain the orders out to the 60 volume per cent acetone if we assume the kinetic expression for the rate is

$$\frac{dx}{dt} = k[U(OH)_2^{2+}][UO_2OH^+] = k \cdot \frac{K_3[U(IV)]}{[H^+]^2\left(1 + \frac{K_3}{[H^+]^2}\right)} \cdot \frac{K_2[U(VI)]}{[H^+]\left(1 + \frac{K_2}{[H^+]}\right)}$$

$$= k \frac{[U(IV)][U(VI)]}{\left(\frac{[H^+]^2}{K_3} + 1\right)\left(\frac{[H^+]}{K_2} + 1\right)} \tag{6}$$

where the expression for the concentrations of UO_2OH^+ is taken from MATHEWS, *et al.*[1] In the limit of $[H^+]^2/K_3$ and $[H^+]/K_2$ each being much larger than unity the reaction would approach an inverse third order dependence on $[H^+]$ and at the same time would be first order with respect to both [U(IV)] and [U(VI)].

The reversal of slope in the 60 volume per cent alcohol solvent (Fig. 3) indicates that the rate is directly proportional to some power of the hydrogen ion concentration in this range of acidity. This is probably due to some complex formation involving hydrogen ion.

As has been pointed out[1,5] the region of 60–70 weight per cent organic component of solvent composition has been found to exert marked influence with respect to chemical kinetic and other phenomena appertaining to ions in solution, and 60–70 volume per cent acetone solvent seems to verify these observations.

While it is not justifiable to average the specific velocity constants given in Table 2 in a given solvent, when the concentrations of highly charged ions and acid vary so widely, and while it is not justifiable to compare the average of the constants in the different solvents since the orders change so drastically, yet a rough idea of the marked effect of the solvent upon the reaction rate constants can be observed by plotting the logarithms of the average of the constants in the different solvents against the volume per cent of acetone in the solvents. Such a plot, assumed to be straight line segments, is given in Fig. 5. The maximum in the plot occurs at about 40–45

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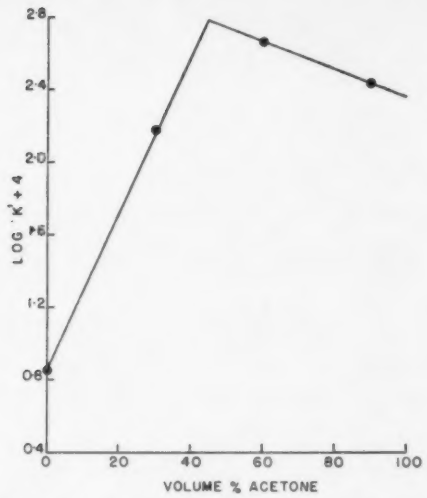

FIG. 5.—Logarithm of the specific velocity constant vs. the volume per cent acetone in the solvent.

volume per cent acetone which is a smaller volume per cent organic component of the solvent than found by MATHEWS *et al.*[1] in the case of the water–ethanol system. In the latter system the maximum occurred at 80–90 volume per cent ethanol.

Our precision in general calculated to be between 5 and 7 per cent. Our care in weighing, volume measurements, counting and analytical procedures were such that we feel that our accuracy was well within the limits of our precision.

Acknowledgements—The authors wish to thank the Atomic Energy Commission for a grant under Contract AT-(40-1)-2069 which made this research possible. Also one of us (S. L. M.) is indebted to the National Science Foundation for an Undergraduate Research Participation Grant.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 334 to 336. Pergamon Press Ltd. Printed in Northern Ireland

COMPLEXES OF DIBUTYL PHOSPHORIC ACID*

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(*Received* 5 *July* 1960; *in revised form* 10 *August* 1960)

Abstract—Highly associated complexes have been formed between dibutyl phosphoric acid and the cations: Cu(II), UO_2(II), Fe(III), Y(III), La(III), Al(III), Th(IV). ^{32}P-labelled dibutyl phosphoric acid was used to assist in the analysis of the compounds. Metathesis of the solid Th(IV) complex with aqueous sodium hydroxide was complete, suggesting a practical method for removing the complexes from solvents and equipment.

DIBUTYL phosphoric acid has been found among the products of many of the reactions of tributyl phosphate (TBP). In extraction processes where TBP is the solvent, small amounts of dibutyl phosphoric acid form undesirable complexes with cations.[1]

The infra-red spectra of many of the DBP complexes with cations have been interpreted by SMITH[2] to show bonding between phosphoryl oxygen atoms and the cation. A more extensive study of bis (2-ethylhexyl) phosphoric acid has been reported by PEPPARD and FERRARO.[3]

Dibutyl phosphoric acid labelled with ^{32}P has been used here to aid in the analysis of the complex compounds, in the measurement of solubility and in following the progress of metathesis reactions. Metathesis of the complexes with aqueous alkali was shown to be complete. The aqueous alkali contained the anion while the residual solid was soluble in nitric acid.

EXPERIMENTAL

Dibutyl phosphoric acid ^{32}P. Tributyl phosphate ^{32}P from the ester interchange reaction[4] was dealkylated with ethanolamine.[5] The resulting acid was purified by distribution between ether and aqueous solutions. A 94 per cent yield was obtained from 0·28 mole TBP. The product (98·8% DBP by titration) contained 0·3 mc ^{32}P per mole. The method of solution counting has already been described.[6]

Preparation of complexes (A). Approximately 10 mmole of the metal nitrate in 20 ml water was stirred vigorously while an aqueous solution of sodium dibutyl phosphate ^{32}P (11 mmole per 10 mmole of nitrate ion) was added drop wise. The filtered solid was washed with water and dried at 76°C under 2 mm Hg pressure. The yields were high for most complexes (see Table 1); however, the copper complex was soluble in the aqueous solution. The original yield (12 per cent) was increased (an additional 46 per cent) by continuous extraction of the aqueous mother liquors. The Cu(II) complex when recrystallized from ethyl acetate or acetone–benzene melted at 118–119°C.

* This paper is based upon work performed for the United States Atomic Energy Commission at the Oak Ridge National Laboratory operated by Union Carbide Corporation.

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(B) A mixture of thorium nitrate (3·8 mmole) and 38·7 mmole dibutyl phosphoric acid in aqueous ethanol was adjusted to pH 1 with 1 M sodium hydroxide. The precipitate was washed several times with hot ethanol and dried *in vacuo*.

(C) Thorium nitrate (20 mmole) in 25 ml distilled water was refluxed for 20 hours with 110 mmole TBP. The volatile liquids were distilled. The precipitate that formed was filtered, washed with methanol and dried *in vacuo*, yield 3·3 g (3·1 mmole, 15 per cent).

^{32}P in the complexes was determined by counting a solution of the complex. Cu(II) complex was dissolved in a mixture of dilute HNO_3 and dioxane; Al(III) complex was miscible in excess NaOH.

TABLE 1.—DIBUTYL PHOSPHATE COMPLEXES

Complex*	Method	Yield	P(%)		Eq. Wt.	
			Found	Calc.	Found	Calc.
CuA_2	A	58	12·8, 12·9	12·9		
UO_2A_2	(†)		9·2‡	9·0	349	344
FeA_3	A	99	13·8	13·6		
AlA_3	A	99	14·3	14·2		
YA_3	A	96			242	239
LaA_3	A	71	18·3‡	18·1	257	256
ThA_4	A				275	267
	B	94	11·5	11·6		
	C				268	

* Where A is $(C_4H_9O)_2P(O)O^-$

† Prepared by B. E. BRYANT by heating an aqueous solution of uranyl nitrate, DBP and urea. Recrystallized from ethanol–benzene.

‡ Ionic; others by radioactivity.

Fe(III), Y(III), La(III), and Th(IV) complexes were treated with three portions of 1 N sodium hydroxide (10 ml/g in each portion). Aliquots from the combined aqueous solutions were counted for ^{32}P activity. The residue from the sodium hydroxide metathesis was dissolved in dilute HNO_3 and was found to contain insignificant amounts of radioactive materials.

The equivalent weight of the complexes was determined by a modification of the method that has been used for the esters.[5] The free acid, that was formed from the complex by exchange with the hydrogen form of cation exchange resin, was titrated potentiometrically with standard sodium hydroxide. The uranyl complex was soluble in ethanol and exchanged rapidly with the resin, thus:

$$UO_2A_{2(l)} + H_2Resin_{(s)} \rightarrow 2HA_{(l)} + UO_2Resin_{(s)}$$

where subscripts l and *s* refer to solution and solid, respectively. The less soluble complexes exchanged too slowly for direct use and were treated, thus:

$$ThA_{4(s)} + 4NaOH_{(l)} \rightarrow Th(OH)_{4(s)} + 4NaA_{(l)}$$

$$NaA_{(l)} + HResin_{(s)} \rightarrow HA_{(l)} + NaResin_{(s)}$$

Equivalent weight = Wt. of complex (g) ÷ equivalents of NaOH needed to neutralize HA liberated by resin.

Theoretical equivalent weight

formula weight of $UO_2A_2 \div 2$

formula weight of $ThA_4 \div 4$

Solubility measurements and metathesis studies were conducted by tumbling the phases, in a glass stoppered centrifuge cone, end over end in a constant temperature bath.

RESULTS

The complexes contained the stoicheiometric amount of dibutyl phosphate required by the valence of the cation. ThA_4 complex was the product that was obtained from all three methods of preparation (see Table 1). The products were often gelatinous

in nature when first formed but were readily obtained as powders when they were washed and dried.

The double decomposition reaction between the complexes and aqueous sodium hydroxide went to completion quite readily. For example 15 ml of 1 N sodium hydroxide per gramme of $Th(DBP)_4$ completely converted the complex in 1 hr at 25°C. Similar results were obtained with La(III) and Fe(III) complexes. $Al(DBP)_3$ completely dissolved during this treatment. $Th(DBP)_4$ was completely miscible in sodium carbonate solution (2 g Na_2CO_3 and 20 ml H_2O per g of complex).

The ease of the metathesis with sodium hydroxide is of practical importance for removing the complexes from plant equipment and from solvents. Treatment with sodium hydroxide solutions will remove the dibutyl phosphate moiety and leave the cation as the hydroxide that is readily soluble in aqueous nitric acid.

The Cu(II) complex was the most soluble, dissolving to the extent of 30 g/l. of water and 18 g/l. of benzene. In benzene the solubility of Fe(III) and Al(III) complexes was less than 1 mg/l. In benzene solution containing 20 per cent TBP the solubility was increased to 40 and 20 mg/l., respectively. Y(III) and La(III) complexes when equilibrated with carbon tetrachloride (3 g/l.) were swelled to a very viscous clear gel.

Cu(II) and UO_2(II) complexes were sufficiently soluble in molten biphenyl to permit the estimation of the molecular weight, cryoscopically. At a concentration of 0·03 formula weight per kg of biphenyl both Cu(II) and UO_2(II) complexes were found to be highly associated (the observed molecular weight exceeded 10,000). The association of the uranyl complex with bis (2 ethylhexyl) phosphoric acid was observed isopiestically by BAES *et al.*[7] and confirmed by PEPPARD and FERRARO.[3]

The DBP complexes with cations of higher valence (3 and 4) have been found to be less soluble than those with divalent cations. The opportunity exists, with cations of higher valence, for the formation of more highly branched polymers.

WARDLAW and BRADLEY[8] have demonstrated the association that exists in the alkoxides of trivalent and tetravalent metals. The role of the size and shape of the alkyl group was shown by them to be important for shielding the cation from association with other molecules. Bis (2 ethylhexyl) phosphoric acid having larger alkyl groups with more branching might be expected to form complexes with less association than those formed from dibutyl phosphoric acid. The co-ordination polymers formed by dialkyl phosphoric acids may well be the result of the phosphoryl oxygen co-ordinating with a cation that is part of a neighboring molecule. The greater the co-ordination number of the cation the greater will be the opportunity to form larger and more complicated structures.

Acknowledgement—The assistance given by A. L. LESLIE during part of this work is greatly appreciated.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 337 to 349. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON MONO- AND DI-n-BUTYLPHOSPHORIC ACIDS—III

THE EXTRACTION OF ZIRCONIUM FROM NITRATE SOLUTION BY DI-n-BUTYLPHOSPHORIC ACID

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(*Received* 12 *August* 1960)

VOL. 17 1961

Abstract—The extraction of $\sim 10^{-6}$ M zirconium from nitrate solution by di-*n*-butylphosphoric acid (HDBP) has been studied as a function of the concentrations of HDBP, nitric acid, nitrate ion, and hydrogen ion. The distribution coefficient for zirconium is proportional to the second power of the final $[HDBP]_{org}$ over the range 10^{-5}–10^{-3} M HDBP, and to the first power of $[NO_3^-]$, and is independent of $[H^+]$ at a constant ionic strength of 2. The mechanism of extraction of zirconium by HDBP, and of other metals by di-alkylphosphoric acids, over a wide range of conditions, is discussed and compared with the mechanism of extraction of zirconium by tributyl phosphate (TBP) and by thenoyltrifluoroacetone (HTTA). The preparation and infra-red spectra of zirconium bis-dibutylphosphate dinitrate are described.

THE significance of certain complexes of zirconium and niobium in solvent extraction processes for the separation of uranium and plutonium has recently been summarised.[1,2] ^{95}Nb and ^{95}Zr are the fission products which largely limit the decontamination factor obtainable in tributyl phosphate (TBP)–nitric acid systems, and the behaviour of these elements in systems containing TBP and its hydrolytic and radiolytic degradation products, mono- and di-butylphosphoric acid (H_2MBP and HDBP respectively), is therefore of importance.

The extraction of zirconium by TBP from nitrate solution has been examined by a number of workers,[3–10] and we have recently reported work on the extraction of niobium by TBP, HDBP, and di(2-ethylhexyl)phosphoric acid (HDEHP).[11] However, little work has been reported on the extraction of zirconium by mono- and di-alkylphosphoric acids, although the extraction of a number of other metals, e.g.

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uranium,[12–14] protactinium,[15–17] plutonium,[18] lanthanides[19–22] and others,[12,21–24] has been examined in detail. SCADDEN and BALLOU[9] found a mixture of H_2MBP and HDBP effective for separating zirconium and niobium from each other and from nearly all other fission product elements in nitric acid–oxalic acid solution, but did not study extraction by the individual acids in detail.

We have extended our previous work[1,11,15] on the extraction of metals by HDBP, and now report details of the extraction of zirconium from nitrate solution as a function of the concentrations of HDBP, nitric acid, nitrate ion, and hydrogen ion; the probable extraction mechanism is also discussed. We also report the preparation and infra-red spectra of zirconium bis-dibutylphosphate dinitrate.

EXPERIMENTAL

Preparation of ^{95}Zr solutions

^{95}Zr tracer stock solutions in 2 M nitric acid were prepared daily from ^{95}Zr–^{95}Nb tracer solution in conc. HF by the paper chromatographic method described in detail previously,[25] and were made 5×10^{-5} M in zirconium by adding inactive zirconium nitrate. Solutions for the distribution experiments were prepared using 0·1 ml aliquots of the stock solution and appropriate concentration of HNO_3, $LiNO_3$, or $HClO_4$, to give 2 ml containing $2{\cdot}5 \times 10^{-6}$ M Zr.

Solvents

HDBP was obtained from Albright and Wilson Ltd., Oldbury, and was shown to be >99·8 per cent pure by electrometric titration and paper chromatography.[25] The inert diluent used was A.R. toluene.

Determination of distribution coefficients for zirconium

The activity of ^{95}Zr in the solvent and aqueous phases was determined by γ-counting aliquots of the phases evaporated to dryness on small stainless steel disks. From preliminary experiments it was shown that distribution equilibrium between the phases was achieved in approximately 2 min. All equilibrations were therefore carried out by stirring equal volumes of the two phases for 5 min at room temperature (20°C) in silicone-treated glass centrifuge tubes, the phases then being separated by centrifugation.

The distribution coefficient for zirconium (D_{Zr}) is defined by: γ-activity of ^{95}Zr in organic phase/γ-activity of ^{95}Zr in equal volume of aqueous phase.

Preparation of zirconium bis-dibutylphosphate dinitrate

A solution of 0·1 M HDBP (containing HDB^{32}P tracer) in toluene was stirred for 1 min with an equal volume of 0·1 M zirconium nitrate in 2 M HNO_3. The phases were separated by centrifugation and the solvent phase stirred with a fresh volume of the zirconium nitrate solution. The phases were again separated by centrifugation and the solvent phase was filtered and analysed for DBP, zirconium, and nitrogen as described below.

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[21] D. F. PEPPARD, G. W. MASON, J. L. MAIER and W. J. DRISCOLL, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
[22] D. F. PEPPARD, G. W. MASON, W. J. DRISCOLL and R. J. SIRONEN, *J. Inorg. Nucl. Chem.* **7**, 276 (1958).
[23] D. F. PEPPARD, S. W. MOLINE and G. W. MASON, *J. Inorg. Nucl. Chem.* **4**, 344 (1957).
[24] D. DYRSSEN, *Acta Chem. Scand.* **11**, 1277 (1957).
[25] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **9**, 322 (1959).

DBP. HDBP in the initial toluene solution was titrated potentiometrically with 0·1 N NaOH, and its specific activity was determined by liquid β-counting of 10 ml of the solution. DBP present in the toluene solution of the zirconium nitrate–dibutylphosphate complex was determined by liquid β-counting of the solution and also by potentiometric titration of the solvent after extraction of the zirconium into 2 M HCl–1 M HF solution.

Zirconium. This was extracted from the solvent phase by stirring in a polythene tube with $\frac{1}{2}$ volume of 2 M HCl–1 M HF. The phases were separated by centrifugation and the aqueous phase washed with toluene and air-sparged. The aqueous phase was made alkaline with 6 M NaOH while stirring, and the precipitated zirconium hydroxide was washed with water and dissolved in 20 ml of 6 M HCl. Zirconium was precipitated as the mandelate complex by adding 15 ml of a 16 per cent solution of mandelic acid and warming to 80°C for 20 min; the precipitate was filtered off, washed with 5 per cent mandelic acid–0·25 N HCl solution, with water, ignited to ZrO_2 and weighed.

Nitrogen. The aqueous alkaline solution from the zirconium hydroxide precipitation was combined with the washings and nitrogen was determined by the standard Kjeldahl method.

Infra-red spectra

The infra-red spectrum of a thin film of the solid zirconium bis-dibutylphosphate dinitrate on a thin silver chloride plate was measured from 2–15 μ on a Hilger H800 double-beam spectrometer equipped with a rock-salt prism. The thin film was obtained by evaporating to dryness a toluene solution of the complex, dissolving the residue in CCl_4, and evaporating this solution on to the silver chloride plate, which was finally dried at 80°C for 10 min. The spectrum of HDBP was measured as a capillary film between sodium chloride plates.

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RESULTS

The variation of D_{Zr} *with* HDBP *concentration*

The variation of D_{Zr} with the initial solvent phase concentration of HDBP over the range 10^{-5}–10^{-3} M HDBP is shown in Fig. 1 for aqueous phases of 2 M and 4 M HNO_3 In these experiments the sum of the final activities in the solvent and aqueous phases agreed to within ± 2 per cent with the initial activity in the aqueous phase. In the experiments at 4 M HNO_3 the ^{95}Zr stock solution was heated for 1 hr at 100° in a sealed glass tube and then centrifuged at high speed for 5 min; the loss in ^{95}Zr was <2 per cent.

The slopes of the log-log plots of D_{Zr} vs. *initial* $[HDBP]_{org}$ are 2·2 and 2·4 for 4 M and 2 M HNO_3 respectively; however, the plot of D_{Zr} for 2 M HNO_3 versus the *final* $[HDBP]_{org}$ gives a slope of 2·0 (Fig. 1). The values of the *final* $[HDBP]_{org}$ were calculated by correcting for

(a) the amount of HDBP complexed with the zirconium in the organic phase assuming a ratio of 1Zr:4HDBP, and
(b) the amount of HDBP in the aqueous phase (due to the relatively low distribution coefficient of HDBP under these conditions).

In the above calculations it was assumed that the values of the dimerisation constant of HDBP in the organic phase, and the distribution coefficients of the monomer and dimer, are the same in the toluene–HNO_3 system as in the benzene–HNO_3 system[27].

The variation of D_{Zr} *with nitrate ion concentration*

The variation of D_{Zr} with nitrate ion concentration at a constant total HDBP concentration (6×10^{-5} M) and constant hydrogen ion concentration (2 M) was studied with perchloric acid–nitric acid mixtures. The results of several duplicate experiments are given in Fig. 2. D_{Zr} is approximately proportional to the first power of the nitrate ion concentration.

[26] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **10**, 323 (1959)
[27] C. J. HARDY and D. SCARGILL, *J. Inorg. Nucl. Chem.* **11**, 128 (1959).

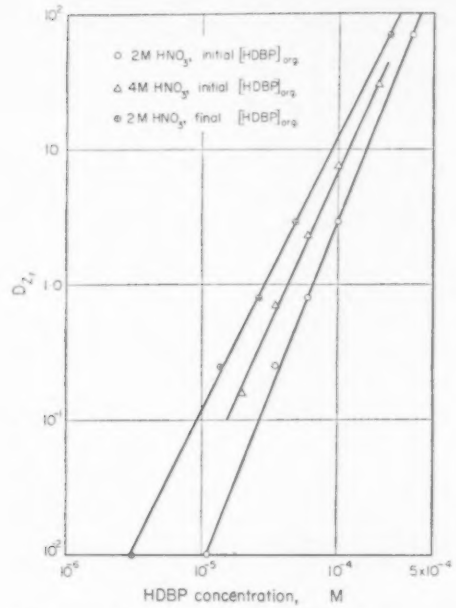

FIG. 1.—The variation of D_{Zr} with HDBP concentration.

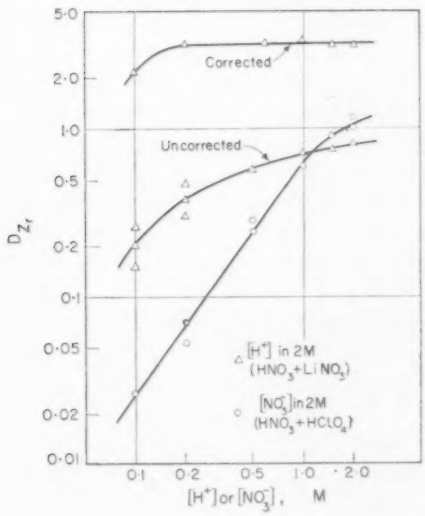

FIG. 2.—The variation of D_{Zr} with hydrogen and nitrate ion concentration at constant ionic strength ($\mu = 2$).

For the equation (IRVING and EDGINGTON[28])

$$\frac{\delta \log D_{Zr}}{\delta \log [NO_3^-]_{aq}} = \bar{n}_{org} - \bar{n}_{aq}$$

[28] H. IRVING and D. N. EDGINGTON, *J. Inorg. Nucl. Chem.* **10**, 306 (1959).

in which D_{Zr} is measured at constant [H^+], [HDBP] and [Zr], $\bar{n}_{org}$ and $\bar{n}_{aq}$ are the average numbers of nitrate ions per zirconium atom in the organic and aqueous phases respectively, the value of $\bar{n}_{org}$ can be inferred. The plot of log D_{Zr} vs. log $[NO_3^-]_{aq}$ (Fig. 2) has a slope of $\sim$1 up to $\sim$1 M $[NO_3^-]$, in which region we can infer from the relevant stability constants[29] (defined by $\beta_n = [Zr(NO_3)_n]/[Zr][NO_3^-]^n$) that $\bar{n}_{aq} \simeq 1$; hence $\bar{n}_{org} \simeq 2$. For values of $[NO_3^-]_{aq}$ greater than 1 M, the value of $\bar{n}_{aq}$ exceeds one and the slope of the curve decreases, thus indicating that the value of two for $\bar{n}_{org}$ is probably maintained (however, the values of the slope and $\bar{n}_{aq}$ cannot be calculated with sufficient accuracy to demonstrate this quantitatively).

D_{Zr} was determined for both uncentrifuged and centrifuged aqueous solutions; the former showed a loss of activity up to 12 per cent in some of the experiments. When the aqueous phases were centrifuged immediately before equilibration the losses were reduced to <5 per cent, and it is assumed from these results that a certain amount of hydrolysis of the zirconium occurred during the preparation of the aqueous phase containing a low concentration of nitrate ions. Further proof of this was obtained by heating a solution of zirconium in 0·1 M HNO_3 for 1 hr at 100°C. A loss of activity of 6 per cent was observed when the solution was centrifuged prior to heating. After heating and re-centrifuging a further loss of 14 per cent of the activity was observed, and prolonged centrifuging caused a further loss of 9 per cent.

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The variation of D_{Zr} with hydrogen ion concentration

The variation of D_{Zr} with hydrogen ion concentration at a constant total HDBP concentration (6×10^{-5} M) and constant nitrate ion concentration (2 M) in lithium nitrate–HNO_3 mixtures was determined for both centrifuged and uncentrifuged stock solutions. The latter solutions showed losses of activity up to 12 per cent and these results were neglected. The centrifuged solutions gave an activity balance of ± 5 per cent above 0·5 M HNO_3, and the results are given in Fig. 2.

D_{Zr} is almost independent of [H^+] over the range 1–2 M [H^+], but is proportional to a low power of [H^+] at <1 M [H^+] (Fig. 2, lower line). It is known however that the distribution coefficient of HDBP decreases considerably as [H^+] decreases from 1 to 0·1 M,[27] and therefore the concentration of HDBP in the organic phase decreases. When the values of D_{Zr} are corrected for this effect (Fig. 2, upper line), assuming that the variation of D_{HDBP} with [H^+] is the same for HDBP in toluene as it is in benzene, and that D_{Zr} is proportional to the total $[HDBP]^2_{org}$, it is seen that D_{Zr} is independent of [H^+].

The variation of D_{Zr} with HNO_3 concentration

The variation of D_{Zr} with HNO_3 concentration from 0·2 to 2 M HNO_3 at 6×10^{-5} M HDBP and from 0·2 to 14 M HNO_3 at 3×10^{-5} M HDBP is shown in Fig. 3. A maximum value of D_{Zr} is observed at about 4 M HNO_3, and D_{Zr} decreases markedly with increasing HNO_3 concentration above 8 M: this behaviour is directly opposite to that found in the extraction of zirconium by TBP.[3]

Summary of experimental results for zirconium in the HDBP–HNO_3 *system*

(i) D_{Zr} is proportional to the final $[HDBP]^2_{org}$ in the range 10^{-6}–10^{-3} M HDBP at constant $[HNO_3]_{aq}$.

[29] *Stability Constants, Vol. 2, Inorganic Ligands*, The Chemical Society, London (1958).

(ii) D_{Zr} is proportional to $[NO_3^-]_{aq}$ in the range 0·1–2 M $[NO_3^-]_{aq}$ at a constant ionic strength of two and constant $[HDBP]_{org}$, and $\bar{n}_{org} \simeq 2$.

(iii) D_{Zr} is independent of $[H^+]_{aq}$ in the range 0·2–2 M $[H^+]_{aq}$ at a constant ionic strength of two and constant $[HDBP]_{org}$.

Composition and infra-red spectra of zirconium bis-dibutylphosphate dinitrate

The saturated solution of the zirconium dibutylphosphate–nitrate complex in toluene gave the following mole ratios of components

$$Zr:DBP:NO_3 \text{ as } 1:2{\cdot}02:1{\cdot}98$$

indicating the composition $Zr(DBP)_2(NO_3)_2$ for the complex under these conditions.

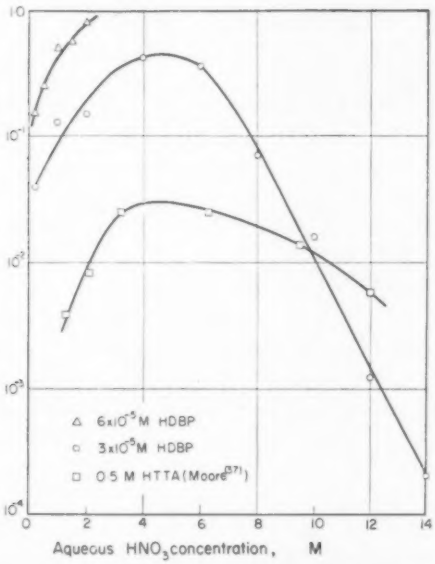

FIG. 3.—The variation of D_{Zr} with HNO_3 concentration.

The infra-red spectra of the solid complex and of liquid HDBP are given in Fig. 4 and the frequencies and probable band assignments in Table 1. The spectrum of HDBP has been reported previously by BELLAMY and BEECHER[30], but the purity of their material is unknown and they did not give frequencies and assignments for all the bands. The spectrum of zirconium tetrakis–dibutylphosphate has been reported by SMITH[31], and of tetrakis-di(2-ethylhexyl)phosphate and of a complex of empirical formula $[ZrO_{0·5}(NO_3)(DEHP)_2]_n$ (where DEHP represents di-2-ethylhexyl phosphate) by PEPPARD and FERRARO[32].

The spectrum of the zirconium bis-dibutylphosphate dinitrate is similar to that of the DEHP-nitrate complex above, bands due to the $—ONO_2$ asymmetric (ν_4) and symmetric (ν_1) stretching vibrations occurring at 1557 cm^{-1} (1553[32]) and 1272–1254 cm^{-1} (1270[32]) respectively. The separation of ν_4 and ν_1 is therefore higher than those for the alkali metal uranyl nitrates and for the uranyl nitrate di- and tri-hydrates

[30] L. J. BELLAMY and L. BEECHER, *J. Chem. Soc.* 728 (1953).
[31] T. D. SMITH, *J. Inorg. Nucl. Chem.* **9**, 150 (1959).
[32] D. F. PEPPARD and J. R. FERRARO, *J. Inorg. Nucl. Chem.* **10**, 275 (1959).

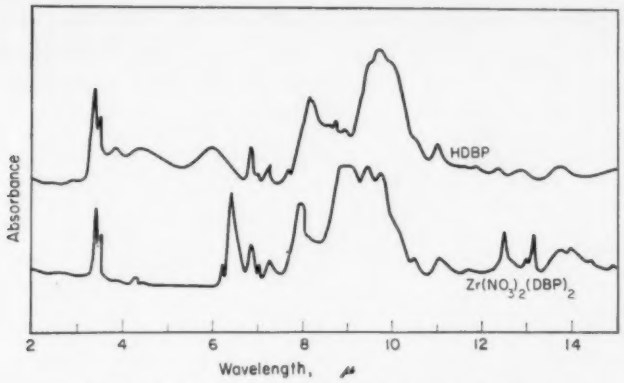

FIG. 4.—Infra-red spectra of HDBP and $Zr(NO_3)_2(DBP)_2$.

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FIG. 5.

studied by GATEHOUSE and COMYNS[33], and by ALLPRESS and HAMBLY[34], in which bidentate nitrate groups are almost certainly present. The shoulder at 1232 cm^{-1} is probably due to a certain amount of the free —P=O group which has largely been shifted from 1228 cm^{-1} in pure HDBP to the region 1120–1130 cm^{-1} in the zirconium complex. This indicates, as pointed out by PEPPARD and FERRARO, that the —P=O group bonds to the metal atom through the oxygen, thus lowering the double bond character of the group. The region 1600–2800 cm^{-1} in pure dibutylphosphoric acid contains three broad bands which have been assigned to the hydrogen-bonded OH

[33] B. M. GATEHOUSE and A. F. COMYNS, *J. Chem. Soc.* 3965 (1958).
[34] J. G. ALLPRESS and A. N. HAMBLY, *Aust. J. Chem.* **12**, 569 (1959).

vibrations[35] which arise from dimerisation. These have completely disappeared in the spectrum of the zirconium complex due to salt formation, indicating that both of the DBP molecules in the complex are bonded to zirconium atoms through the oxygen

TABLE 1.—INFRA-RED SPECTRA OF HDBP AND $Zr(NO_3)_2(DBP)_2$

Frequencies of bands (cm^{-1})		Probable assignment
HDBP	$Zr(NO_3)_2(DBP)_2$	
2941 *m**	2932	C—H stretch
2905 *sh*	2905	
2847 *w*	2847	
2587 *w, b*		ν O—H
2271 *m, b*		ν O—H
1685 *s, b*		δ O—H
	1604 *w*	NO_2 asym. stretch (ν_4)
	1557 *s*	
1463 *w*	1462 *w*	CH_3 degen. deform.
1430 *vw*	1429 *vw*	
1377 *w*	1377 *w*	CH_3 sym. deform.
1299 *vw*		
	1272 *s*	NO_2 sym. stretch (ν_1)
	1254 *s*	
1228 *s, b*	1232 *vw*	P=O stretch
1166 *vw*		
1149 *vw*		
1121 *vw*	1120 *s, b*	P—O stretch
	1104 *s*	
1059 *s*	1065 *s*	P—O—C stretch
1032 *s*	1032 *s*	
1011 *sh*		
	1000 *sh*	N—O stretch (ν_2)
960 *sh*	955 *w*	
909 *w*	909 *w*	CH_3 wag
845 *vw*	854 *vw*	
809 *w*		
	802 *w, sp*	nitrate non-planar rock (ν_6)
777 *w*	771 *w*	
	763 *w, sp*	NO_2 sym. bend (ν_3)
729 *w, b*	728 *w, b*	
	715 *w*	NO_2 asym. bend (ν_5)

* *s* = strong, *m* = medium, *w* = weak,
v = very, *sp* = sharp, sym. = symmetric,
asym. = asymmetric, *sh* = shoulder.

of the acidic OH group. The region 1000–1065 cm^{-1} has bands due to the O—C and O—P vibrations of the P—O—C groups in both the free acid and in the complex. The bands are better resolved in the complex, probably due to the elimination of the hydrogen-bonding which can occur in the free acid.

[35] J. T. BRAUNHOLTZ, G. E. HALL, F. G. MANN and N. SHEPPARD, *J. Chem. Soc.* 868 (1959).

DISCUSSION

Mechanism of extraction of zirconium from HNO_3 *solution by* HDBP *and probable structures of the complexes*

The four general types of behaviour (Types 1, 2, 3 and 4) which have been distinguished by previous workers for the extraction of metals by dialkylphosphoric acids (HX) are summarised in Table 2.

In the most usual type of behaviour (Type 1) the formation of the complex is assumed to take place through the reaction of the metal cation with mono-ionized dimers of the alkylphosphoric acid, since dimers have usually predominated in the organic phase under the experimental conditions.

PEPPARD and co-workers have shown[32,36] that several metals can be extracted from nitrate solution by HDEHP as mixed complexes containing nitrate, as opposed to the complexes which are usually extracted from a weakly complexing aqueous phase, e.g. perchlorate. They postulate, for Th^{4+} for example,[36] co-existent equilibria (equations (4a) and (4b), Table 2) and show that only one nitrate is present per thorium atom in the organic phase. Whether an anion-containing species is extracted depends upon the nature of the anion, the nature of X, the concentration of $(HX)_2$ in the solvent phase, and the acidity of the solvent phase. They also show by saturation experiments[32] that one nitrate per atom of tetravalent Th, Ce, Zr and Hf, can be obtained under appropriate conditions.

We have now shown by solvent extraction experiments at tracer levels of zirconium that two nitrate groups and two DBP dimers are associated with each zirconium atom in the organic phase of the HDBP–toluene–HNO_3 system. Also, D_{Zr} is independent of $[H^+]$ in the aqueous phase. We therefore interpret the mechanism of extraction of zirconium under these conditions by equation (5):

$$ZrO^{2+} + 2(HDBP)_2 + 2NO_3^- \rightleftharpoons [Zr(NO_3)_2(DBP.HDBP)_2] + H_2O \qquad (5)$$

and postulate that the complex probably has the structure I with bidentate NO_3 groups and octa-co-ordination rather then monodentate NO_3 groups and hexa-co-ordination. Our explanation of the decrease of D_{Zr} as $[HNO_3]$ is increased above about 4 M is that:

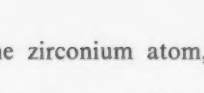
(i) nitrato complexes such as $ZrO(NO_3)_2$, or $Zr(NO_3)_4$, and $H_2Zr(NO_3)_6$, become the predominant species in the aqueous phase and compete with the formation of the DBP complex, and (ii) the amount of free HDBP is reduced as $[HNO_3]$ is increased due to the formation of the $HDBP.HNO_3$ complex (cf. the $TBP.HNO_3$ complex).

The solvent extraction data indicate that the complex at low zirconium concentration has two dimers (DBP.HDBP) per Zr atom, e.g. structure I, but as saturation is approached the composition of the complex tends towards $Zr(NO_3)_2(DBP)_2$ and evaporation of the solution gives a white polymeric solid of no definite X-ray pattern. The structure of the complex in the saturated solution and in the solid may be a three dimensional network of zirconium atoms joined together with single DBP molecules (structure II) or it may be a chain of zirconium atoms each pair of which are linked by two DBP molecules (structure III). Termination of the chains could occur through free P=O and P—OH groups, or by one DBP molecule forming a four-membered

[36] D. F. PEPPARD, G. W. MASON and S. MCCARTY, *J. Inorg. Nucl. Chem.* **13**, 138 (1960).

TABLE 2.—DEPENDENCE OF D_M ON THE CONCENTRATIONS OF HX, H^+ AND ANION

Type	Cationic species	Dependence of D_M on power of concentration			References	Postulated extraction mechanism
		$[HX]_{org}$ at constant $[H^+]_{aq}$	$[H^+]_{aq}$ at constant $[HX]_{org}$	$[anion]_{aq}$ at constant $[HX]_{org}$		
1	UO_2^{2+}	2	−2 (at low $[H^+]_{aq}$)	Independent	12–14	$M_{aq}^{n+} + n(HX)_{2,org} \rightleftharpoons M(HX_2)_{n,org} + nH_{aq}^+$ polymerization ↓ $M_Z X_{2Z+2} H_2$ equation (1)
	La^{3+}, etc.	3	−3	Independent	19–22	
	$Nb(OH)_x^{(5-x)+}$	~3	~−2(at low $[H^+]_{aq}$)	Independent	11	
	Pu^{4+}	4	−4	Independent	18	
2	UO_2^{2+}	2	independent at high $[H^+]_{aq}$	2 (at high $[H^+]_{aq}$)	1	$M_{aq}^{n+} + nNO_3^- + p(HX)_{2,org} \rightleftharpoons$ $M(NO_3)_n(HX)_{2p,org}$ equation (2)
	$Nb(OH)_x^{(5-x)+}$	~3			11	
3	$Pa(OH)_x^{(5-x)+}$	2	1	Independent	16,17	$[Pa(OH)_3X_3]_{aq}^- + 2HX_{org} + H_{aq}^+ \rightleftharpoons$ $PaX_{3,org} + 3H_2O$ equation (3)
4	Th^{4+}	3	−3 or −4	1 or independent	36	$M_{aq}^{4+} + 3(HX)_{2,org} \rightleftharpoons MX_2(HX_2)_{2,org} + 4H_{aq}^+$ equation (4a) $MA_{aq}^{3+} + 3(HX)_{2,org} \rightleftharpoons$ $MA(HX_2)_{3,org} + 3H_{aq}^+$ equation (4b)
5	$Zr(OH)_x^{(4-x)+}$	2	Independent	1	This work	—

ring with one zirconium atom, e.g.  , instead of a linear or ring structure with two atoms of zirconium.

Comparison of the extraction of zirconium from HNO_3 *solution by* HDBP, HTTA *and* TBP

The present results on the extraction of zirconium from HNO_3 by HDBP are compared below with those for the extraction by HTTA from HNO_3[37] and from $HClO_4$,[38] and those for the extraction by TBP from HNO_3.[3]

Complexing agent	Ref.	Aqueous phase	Dependence of D_{Zr} in			
			1–4 M acid			>4 M acid
			(Complexing agent)	$[H^+]$	$[NO_3^-]$	$[HNO_3]$
HTTA	38	$HClO_4$	4	3	—	—
HTTA	37	HNO_3	2	$[HNO_3]^2$		decreases (see Fig. 3)
HDBP	this work	HNO_3	2 (as dimer)	0	1	decreases strongly (see Fig. 3)
TBP	3	HNO_3	2	$[HNO_3]^2$		increases strongly

The results of CONNICK and MCVEY[38] were explained by the reaction

$$Zr(OH)_n^{4-n} + 4HTTA \rightleftharpoons Zr(TTA)_4 + (4 - n)H^+ + nH_2O \quad (6)$$

and the species $Zr(OH)^{3+}$ was considered to predominate in the aqueous phase. The work of MOORE[37] shows that a different mechanism is followed in a nitric acid system.

The results for the extraction of zirconium from 1–4 M HNO_3 by HTTA, HDBP and TBP are similar in their dependence on $[NO_3^-]$ or $[HNO_3]$, but differ in the magnitude of D_{Zr}. The concentrations of HDBP, HTTA and TBP required to give equivalent extraction of zirconium from 2 and 10 M HNO_3 are compared in Table 3. The concentration of HDBP required to obtain a given D_{Zr} is 10^2–10^3 less than the concentration of HTTA, and 10^3–5×10^4 less than the concentration of TBP.

It seems very probable that the complex extracted into the organic phase in the HTTA–HNO_3 system contains two nitrate groups and two TTA molecules and has the structure $Zr(NO_3)_2(TTA)_2$ with bidentate nitrates and octa-co-ordination around the Zr atom. In the $HClO_4$ system however the complex in the organic phase appears to be $Zr(TTA)_4$ with four chelated rings and octa-co-ordination.

In the TBP–HNO_3 system the complexes $Zr(NO_3)_4(TBP)_2$[3] and $Zr(NO_3)_4(TBP)$[4] have been postulated. It seems likely however that TBP extracts to different extents a number of species ranging from $Zr(OH)_2(NO_3)_2(TBP)_2$ to $H_2Zr(NO_3)_4(TBP)_2$.

Comparison of the structures of complexes of zirconium with dialkylphosphates and β-diketones under various conditions

A comparison of the various zirconium dialkylphosphate–nitrate complexes referred to above with the zirconium β-diketone–nitrate complexes prepared by

[37] F. L. MOORE, *Analyt. Chem.* **28**, 997 (1957).
[38] R. E. CONNICK and W. H. MCVEY, A.E.C.D.-2272 (1948).

TABLE 3.—CONCENTRATIONS OF TBP, HTTA AND HDBP TO GIVE EQUIVALENT EXTRACTION OF Zr FROM HNO_3 SOLUTION

(a) $D_{Zr} = 0{\cdot}2$ at 3 M HNO_3

Solvent	Diluent	Concentration (M)	Ref.
TBP	Kerosene	1·38	3
HTTA	Xylene	$2{\cdot}45 \times 10^{-2}$*	37
HDBP	Toluene	3×10^{-5}	This work
Ratio $\frac{[TBP]}{[HDBP]} \simeq 5 \times 10^4$; $\frac{[HTTA]}{[HDBP]} \simeq 10^3$			
(b) $D_{Zr} = 10^{-2}$ at 10 M HNO_3			
TBP	Kerosene	$2{\cdot}7 \times 10^{-3}$	3
HTTA	Xylene	5×10^{-3}*	37
HDBP	Toluene	3×10^{-5}	This work
Ratio $\frac{[TBP]}{[HDBP]} \simeq 10^3$; $\frac{[HTTA]}{[HDBP]} = 1{\cdot}6 \times 10^3$			

* Calculated assuming $D_{Zr} \propto [HTTA]^2$ from data at 0·5 *M* HTTA

BRAININA *et al.*[39] or studied by MOORE[37] and CONNICK and MCVEY[38] shows that in such systems the structure of the complex obtained depends markedly on the conditions of its preparation. Similar effects will probably occur with many other metals in similar systems.

Formula	Name	Reference	Conditions
$Zr(DBP)_4$	Tetrakis-DBP	SMITH[31]	Pptn. from dil. aq. acid.
$Zr(DEHP)_4$	Tetrakis-DEHP	PEPPARD[32]	Extn. from aq. neutral chloride soln. to give satd. soln. in toluene.
$ZrO_{0\cdot5}(NO_3)(DEHP)_2$	—	PEPPARD[32]	Extn. from aq. neutral nitrate soln. to give satd. soln. in toluene.
$Zr(NO_3)_2(DBP)_2$	Bis-DBP dinitrate	This work	Extn. from 0·1 M Zr soln. in 2 M HNO_3 into toluene.
$Zr(NO_3)_2(DBP.HDBP)_2$	—	This work	Inferred in soln. from solvent extn. data.
$Zr(NO_3)_2(A)_2$	Bis-acetylacetonate dinitrate*	BRAININA[39]	Heated acetylacetone + $ZrO(NO_3)_2$ in benzene.
$Zr(NO_3)_2(TTA)_2$	Bis-TTA dinitrate	This work	Inferred in soln. from data in ref. (37).
$Zr(NO_3)(A)_3$	Tris-acetylacetonate mononitrate*	BRAININA[39]	Heated acetylacetone + $ZrO(NO_3)_2$ in benzene with sodium bicarbonate.
$Zr(A)_4$	Tetrakis-acetyl-acetonate*	BRAININA[39]	Pptn. or extn. from aq. soln.
		CONNICK and MCVEY[38]	Inferred in soln. from extn. data

* Similarly with benzoylacetone.

[39] E. M. BRAININA, R. KH. FREIDLINA and A. N. NESMIANOV, *Bull. Acad. Sci. U.S.S.R.* (8) 910 (1958).

BRAININA *et al.* report[39] that the zirconium β-diketone mono- and di-nitrates are colourless crystalline compounds, soluble in benzene, dioxane, $CHCl_3$, and toluene, and give mono-solvates from solution. They are unstable towards water and recrystallisation from water leads to extensive hydrolysis. It therefore seems likely that the $[ZrO_{0.5}(NO_3)(DEHP)_2]_n$ complex prepared by PEPPARD and FERRARO[32] was formed by hydrolysis from a dinitrato complex (cf. $Zr(NO_3)_2(DBP)_2$) when the organic solution was washed with water. The range of nitrate to zirconium ratios (0·6–1·2) found by PEPPARD and FERRARO (for washed and non-washed organic phases respectively) provides further support for this hypothesis. Their preparations did not exceed a ratio of 1·2 because they used a non-acidified aqueous solution of zirconium nitrate, in which considerable hydrolysis had probably already occurred.

The effect of HDBP *on the extraction of zirconium by* TBP

In TBP processes for the separation of uranium and plutonium from fission products the formation of HDBP (and also H_2MBP) as a degradation product of TBP by hydrolysis and radiolysis can cause

(a) reduced decontamination factors for zirconium and niobium;
(b) retention in the solvent (after stripping) of uranium, plutonium, zirconium, and niobium; these complicate solvent recycling and may add to effluent treatment problems; and
(c) the precipitation of material which contains uranium leading to a loss of this element as well as trouble through emulsification of organic and aqueous phases.

The practical effect of small amounts of HDBP on the extraction of zirconium by TBP can be seen when one considers that about 36 mg HDBP/l.hr is formed when 20% TBP in contact with uranyl nitrate in nitric acid is subjected to a radiation level of 1 w/l. from mixed fission products;[1] this amount represents $1{\cdot}8 \times 10^{-4}$ M HDBP.

Values of D_{Zr} for the extraction of trace zirconium by 20% TBP (0·69 M) are 0·05 at 2 M HNO_3 and 0·23 at 4 M HNO_3.[3] Corresponding values of D_{Zr} for HDBP extraction under similar conditions are given by 2×10^{-5} M HDBP, and this represents only 3×10^{-3} vol per cent impurity. At high concentrations of HNO_3, e.g. >10 M, the effect of small amounts of HDBP is relatively less than at low acidity, but is still considerable.

Acknowledgements—The authors wish to thank Dr. J. M. FLETCHER and Mr. J. KENNEDY for many helpful discussions.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 350 to 360. Pergamon Press Ltd. Printed in Northern Ireland

GROUP SEPARATION OF THE ACTINIDES FROM THE LANTHANIDES BY ANION EXCHANGE*†

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(*Received* 16 *June* 1960)

Abstract—The separation of the lanthanides from the tripositive actinides has been successfully accomplished by column elution with lithium chloride solutions 10 M or stronger using a moderately cross-linked, strongly basic anion exchange resin at an elevated temperature. Fractionation of the actinide ions into the groups Pu, Am–Cm, Bk, and Cf–Es can be obtained during the same column elution.

The distribution coefficient D_v (defined in terms of the geometric resin bed volume) of representative actinides and lanthanides was investigated as a function of LiCl and H^+ concentration, temperature, and cross-linkage of the resin, using the column elution technique. In addition, adsorption kinetics were investigated by measurement of americium elution peak half-widths over a range of flow-rates at 25 and 87°C with 2, 8, and 10 per cent DVB resin of several particle sizes.

The formation of anionic complexes is markedly influenced by the LiCl and H^+ concentrations. D_v for La, Lu, Am and Cf uniformly decreased by nearly one-fourth when the H^+ concentration was increased from 0·1 to 1·0 M, while maintaining the chloride ion concentration constant at 10·15 M. Except for deviations observed in the elution order of Gd and Ho and their corresponding actinide homologs, Cm and Es, the elution sequence proceeded in order of increasing atomic number, La being the least strongly adsorbed. Under acceptable operating conditions the ratio $D_v(\text{Am})/D_v(\text{La}) = 19$.

DURING the past six years a new separation method has evolved for the group separation of the tripositive actinides from the lanthanides. This method is based on the finding that the lanthanides, as a group, elute prior to the actinides from a strong base anion exchange resin, using a highly concentrated solution of lithium chloride as eluant.[1a,1b] This communication presents data from an intensive study of this system.

Earlier information suggested that the chloride ion was singular in yielding more extensive complex formation with the actinides than the lanthanides. For an example, from concentrated HCl the transuranic elements are more strongly adsorbed than the lanthanides by anion exchange resin.[2] The reverse order of adsorption is well known for cation exchange resin.[3,4] Lithium chloride solutions were expected to behave similarly on the basis that solutions of LiCl and HCl of equal molalities have nearly equal thermodynamic activities. Nevertheless, GRAY found in preliminary experiments that the adsorption of americium by Dowex-1 anion exchange resin was considerably greater from LiCl solutions than from HCl of the same concentration.[1a] Independent work by KRAUS *et al.*[5] likewise revealed greater adsorption from LiCl

* Work done under the auspices of the U.S. Atomic Energy Commision.

† Reported in part at *The XVII International Conference of Pure and Applied Chemistry*, Munich, 1959, by E.K.H.

(1) (a) K. STREET, JR. and P. GRAY, U.S. Pat. Application, File No. 724–487. (b) See also, J. J. KATZ and G. T. SEABORG, *The Chemistry of the Actinide Elements*, pp. 339, 346 and 363. Methuen, London, (1957).
(2) S. G. THOMPSON, B. G. HARVEY, G. R. CHOPPIN and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 6229 (1954).
(3) K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **72**, 2790 (1950).
(4) R. M. DIAMOND, K. STREET, JR. and G. T. SEABORG, *J. Amer. Chem. Soc.* **76**, 1461 (1954).
(5) K. A. KRAUS, F. NELSON, F. B. CLOUGH and R. C. CARLSTON, *J. Amer. Chem. Soc.* **77**, 1391 (1955).

solutions than from HCl for many metal ions. Although this behaviour could not be interpreted, use was made of it at this laboratory, where applications have included the separation of rare earth fission products from neutron irradiated Pu, Am and Cm respectively,[6] and the separation of La from gramme amounts of ^{241}Am.[7]

The usefulness of the LiCl-anion exchange system having been demonstrated, it was decided to investigate its basic aspects in the present study. Separation factors and elution positions under widely varying conditions are predictable from the data obtained. An unexpected bonus was the finding that ions of Bk, Cf, and Es are adsorbed by the resin to an extent sufficient to isolate them from the lighter actinides. Thus, under proper conditions, a single elution will fractionate the tripositive actinides in addition to separating the rare earth fission products. Aside from these results, interesting information concerning the ion-exchange behaviour of the lanthanides and transuranic elements has been produced.

The column elution technique was used to measure the distribution coefficients for a number of elements simultaneously under identical conditions. The following factors were successively investigated: effects of flow rate, effects of resin cross-linkage and temperature on adsorption and selectivity by the resin, and the variation of adsorption with concentrations of HCl and LiCl. These studies ascertained the optimum conditions for actinide-lanthanide separations and for maximum practical resolution of elution peaks from adjacent ones. Using these conditions, the elution order and positions of all the lanthanides and tripositive actinides available to us were determined.

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EXPERIMENTAL

Apparatus

Ion-exchange columns were of 6 mm or 10 mm inside diameter, with temperature jacketing. For experiments at 87°C the vapour of trichloroethylene was circulated through the jacket. Between room temperature and 87°C, constant temperature (±0·2°C) was maintained by circulating water from a thermostated bath. The height of resin in the column was between 10 and 12 cm. To prevent floating of the resin, a thin "sheet" of glass wool was placed on top of the resin bed. Associated apparatus consisted of a 100 ml calibrated burette for accurate metering of the LiCl eluant, a precision air pressure regulator to achieve the desired flow rates, a photoelectric drop-counter, and a turntable carrying 3 ml test tubes.

Resin

The anion exchange resins employed were Dowex-1 in the chloride form with a divinylbenzene (DVB) content (or proportionally, the cross-linking) ranging from 2 to 10 per cent. A hydraulic grading method was used to obtain a fraction of the stock with the desired settling rate in water (usually 8–15 mm/min). A coarser particle size, used in one study, had a settling rate of 30–70 mm/min. The resins, other than several analytical grade lots obtained from Bio-Rad Laboratories, were conditioned by alternately washing with hydrochloric acid and water.

Solutions and reagents

A stock LiCl solution (approximately 12 M) was prepared from reagent grade LiCl and distilled water. Slight amounts of metal ion impurities present were removed by slow passage through a Dowex-1, 10% DVB resin bed, yielding a pure colourless solution. From the LiCl stock solution various concentrations of slightly acidified LiCl were made by dilution and addition of redistilled HCl (see Table 1). Final concentrations of H^+ and total Cl^- were determined by titration with standard base and $AgNO_3$ solutions, respectively.

[6] G. H. Higgins and W. W. T. Crane, U.S. Pat. 2 887 358 (1959).
[7] R. W. Hoff. Unpublished work.

The transuranic tracers used in this study were ^{239}Pu ($2{\cdot}44 \times 10^4$ years), ^{241}Am (458 years), ^{244}Cm (17·5 years), ^{249}Bk (323 days), $^{250-252}$Cf (10 years, 2·2 years), and ^{253}Es (20 days). ^{239}Pu and ^{241}Am are obtainable from the Isotope Division of Oak Ridge National Laboratory, Oak Ridge, Tennessee. The other tracers were produced by the authors from long neutron irradiations of ^{242}Pu. Purities of the tracers were normally established by α-energy determinations from α-pulse-height-analyses. ^{249}Bk, which has a 10^{-3} per cent α-branching ratio, was characterized by the emission of soft β^- particles and by its elution position from cation resin columns.

The stable elements were used to determine elution positions of the lanthanides. For this purpose, two solutions were prepared from Johnson-Matthey spectrographically pure rare earth oxides at

TABLE 1.—COMPOSITION OF LiCl ELUANTS

Solution	LiCl (M/l.)	HCl (M/l.)
A	9·92	0·1063
B	10·15	0·0099
C	10·15	0·0501
D	9·94	0·260
E	9·66	0·490
F	9·17	0·962
G	8·03	0·0994
H	8·85	0·0978
I	10·98	0·0953
J	11·68	0·0857

total metal ion concentrations of 32 g/l. in approximately 10 M LiCl. One solution contained La and Lu, and the other all of the stable rare earths. Though macroscopic amounts of the rare earths were used, the column resin loadings never exceeded 2 per cent of the bed capacity, assuming a uni-negative charge of the complex.

Procedure

The method of starting and performing a column elution was typical of that employed in earlier studies.[2] Fractionation of the eluate was accomplished by automatic indexing of the tube turntable by the drop-counter control unit, after a predetermined number of drops had been collected in a tube.

By correlation of the number of drops collected with the volume of LiCl solution expended during an elution, the volume of each fraction could be calculated within a standard error of 0·2 per cent. For values of $D_v > 3$ the eluate volume to peak maximum was reproducible within 3 per cent. From the volume of eluate required to reach a peak maximum, a distribution coefficient, D_v, was calculated in terms of geometric resin bed volumes. Based on a theoretical analysis by GLUECKAUF,[8] the relationship is $D_v = (\bar{v}/X) - \alpha$ where $\bar{v}$ = eluate volume to peak maximum, X = geometric resin bed volume, and α = fractional bed void. The designation D_v, used by others,[9] has been substituted for the equivalent K_D used by GLUECKAUF to avoid confusion with the K_D defined by MAYER and TOMPKINS.[10] The total bed volumes and fractional bed voids are determined after equilibration with eluant. By experiment the fractional bed void was established as 40–50 per cent of the geometric resin bed volume, but the 50 per cent value was used for consistency throughout this study.

^{241}Am and ^{252}Cf analyses were carried out by scintillation counting of liquid samples in a well-type NaI(Tl) crystal. The modes of decay of the other transuranic tracers are such that very few photons are emitted, thereby requiring α-particle counting and α-pulse-analysis to be used. For these elements, a chemical separation from the LiCl solution was necessary before radiometric analysis. The separation chemistry performed on each fraction consisted of a hydroxide precipitation with iron carrier, dissolution of the precipitate in 6 M HCl and extraction of the iron with methyl isobutyl ketone. Usually, the total volume of HCl was evaporated and the residue ignited on a platinum disk for

[8] E. GLUECKAUF, *Trans. Faraday Soc.* **51**, 34 (1955).
[9] See for example, K. A. KRAUS, F. NELSON and G. W. SMITH, *J. Phys. Chem.* **58**, 11 (1954).
[10] S. W. MAYER and E. R. TOMPKINS, *J. Amer. Chem. Soc.* **69**, 2866 (1947).

α-counting, but, to resolve overlapping peaks, thin volatilized samples were often prepared for α-pulse-analysis. Total α-particle count rates were obtained in a 2π-geometry α-counter, while ^{249}Bk was counted in a windowless proportional counter.

The concentration of the lanthanides present in a fraction was established spectrographically, subsequent to removal of LiCl by the above chemistry. The solutions resulting from the separation were diluted to 1 ml, and a 0·1 ml aliquot was placed on two flat, paraffin-coated graphite electrodes, evaporated, and excited in an a.c. spark. The intensities of the spectra obtained were compared with those obtained from standard solutions. The error in the location of a lanthanide elution peak, which is dependent on the relative size of the eluate fraction and distribution coefficient, is estimated to be 4–20 per cent.

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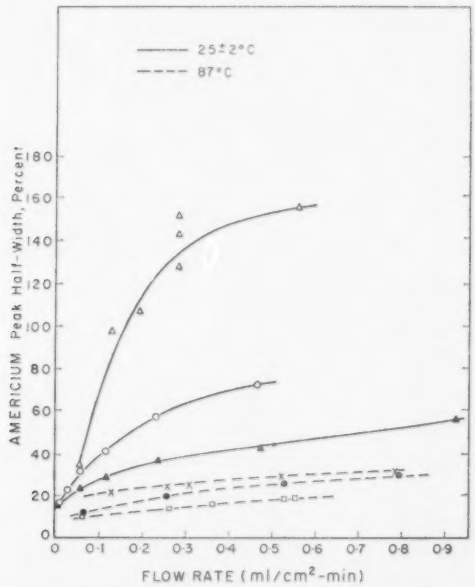

FIG. 1.—Americium elution peak half-width vs. flow-rate.
△ Dowex-1, 10% DVB, 30–70 mm/min settling rate in water.
○, ● Dowex-1, 10% DVB, 7–20 mm/min settling rate in water.
×, ▲ Dowex-1, 2% DVB, 20–70 mm/min settling rate in water.
□ Dowex-1, 8% DVB, 8–15 mm/min settling rate in water.

RESULTS AND DISCUSSION

A. *Effects of flow-rate*

An ion-exchange technique is valueless as a method of separation if the resolution of the elution peaks is poor. In an effort to minimize peak widths and to determine if rate problems existed, the americium elution peak half-width was measured over a suitable range of flow-rates as a function of temperature, resin particle size and resin cross-linking. The results summarized in Fig. 1 are valid only for americium and the conditions employed. Half-widths are defined as full peak widths at half maximum and are expressed as a percentage of the volume of eluate required for the solute to reach maximum concentration.

The results are consistent with a rate of exchange controlled by particle diffusion;[11,12] increase of temperature, finer resin particle sizes, and higher porosity

[11] G. E. BOYD, A. W. ADAMSON and L. S. MEYERS, *J. Amer. Chem. Soc.* **69**, 2836 (1947).
[12] D. REICHENBERG, *J. Amer. Chem. Soc.* **75**, 589 (1953).

resins tended to decrease half-widths. In some instances there was no proximity to equilibrium, such as at 25°C where D_v (Am) was a function of flow-rate using Dowex-1, 10% DVB (7–20 ml/min settling rate); however, at 87°C flow rates up to 0·8 ml/cm² min had no effect on D_v (Am). A limiting half-width of 8–10 per cent is indicated by the converging curves in Fig. 1, which is probably due to slight disturbances of the resin band on which the tracers are loaded and to nonlaminar (channelling) flow through the resin bed. Of the resins tested, Dowex-1, 8% DVB, gave the best performance and was used in most of the succeeding experiments at flow rates of 0·30–0·56 ml/cm² min.

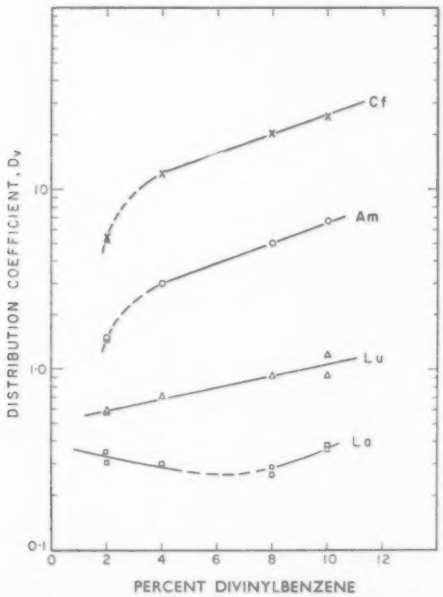

FIG. 2.—Variation of distribution coefficients with resin cross-linking. Elutions made with LiCl solution A (Table 1) at 87°C.

B. *Adsorption vs. resin cross-linking and temperature*

Since the selectivity and adsorption qualities of an ion-exchange resin are dependent on the amount of resin cross-linking,[13] distribution coefficients of selected actinides and lanthanides were measured using Dowex-1 resins of various cross-linkages. The results shown in Fig. 2 indicate that at constant capacity the selectivity, with regard to group separations, uniformly increased with cross-linking. Although the results were predictable qualitatively, the marked convergence of the actinide–lanthanide series with 2% DVB resin was unexpected. However, this was verified with two different batches of 2% DVB resin.

Due to the marked influence of temperature on the rate of exchange in column elutions, it was important to determine the temperature-dependence of the distribution coefficient for several representative actinides and lanthanides. Elutions of americium from Dowex-1 resin, varying in DVB content from 2 to 10 per cent, were carried out at room temperature and 87°C. It is interesting to note that the specific temperature-dependence is a function of the amount of resin cross-linking (Fig. 3). Dowex-1, 8%

[13] See e.g., S. LINDENBAUM, C. F. JUMPER and G. E. BOYD, *J. Phys. Chem.* 63, 1924 (1959).

DVB, was chosen for further study of the elution positions of La, Lu, Am and Cf as a function of temperature. The greater temperature-dependence of the actinides as compared with the lanthanides is shown in Fig. 4, where ln D_v is plotted vs. the reciprocal of the absolute temperature. Use of elevated temperatures clearly improves the actinide–lanthanide separation, in addition to reducing peak half-widths.

At a given temperature the slopes of the curves or d(ln D_v)/d(1/T) shown in Figs. 3 and 4 are proportional to the combined apparent partial molal heats of the reactions

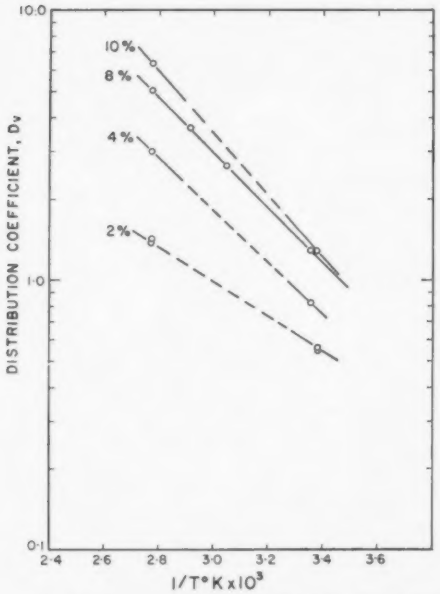

FIG. 3.—Effect of resin cross-linking upon the temperature-dependence of the americium distribution coefficient. Divinylbenzene content of Dowex-1 resins shown as percentages. Elutions performed at room temperature and 87°C with LiCl solution A (Table 1).

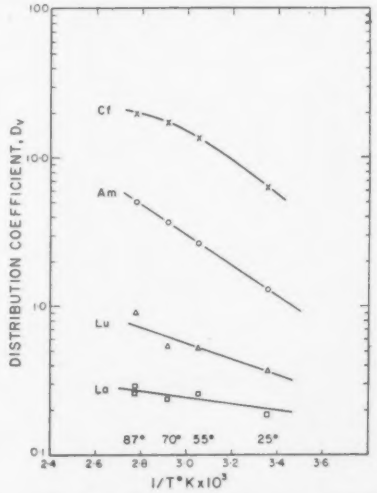

FIG. 4.—Temperature-dependence of the distribution coefficients of americium, californium, lanthanum and lutecium. Resin bed = 6 mm diam × 11·2 cm, Dowex-1, 8% DVB. LiCl solution A (Table 1) was used.

($\Delta H'$) involved.[14] These reactions are presumed to include the formation of negatively charged complexes and their exchange by anion exchange resin. In this investigation positive heats of reaction were found, whereas negative values have been reported in other anion exchange studies.[15] It therefore appears difficult to anticipate the effects of temperature, though most complexing proceeds with negative heats of formation which would be expected to predominate over heats of ion-exchange.

C. *Effect of* HCl *and* LiCl *concentrations*

Due to the interesting difference in complexing properties of HCl and LiCl solutions, the effect of varying the acidity of the LiCl elutriant should be pronounced. In Fig. 5 the results are presented for a number of elutions where Li^+ was progressively

[14] G. N. LEWIS and M. RANDALL, *Thermodynamics and the Free Energy of Chemical Substances*, p. 298. McGraw-Hill Book, New York (1923).
[15] J. P. SURLS, JR. and G. R. CHOPPIN, *J. Inorg. Nucl. Chem.* **4**, 62 (1957).

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replaced with H^+, maintaining a constant ionic strength of 10·15 M. Since in preparation slight variations in solution concentrations occurred, some elution data were later normalized to the above ionic strength.

Adsorbability of the actinide and lanthanide ions markedly decreased with increasing acidity and adsorption appeared to be solely dependent on the decreasing concentration of LiCl, in the range of 0·1–1·0 M HCl (compare Am and Cf in the 9–10 M LiCl range in Fig. 6). No clear explanation is evident for such behaviour, but

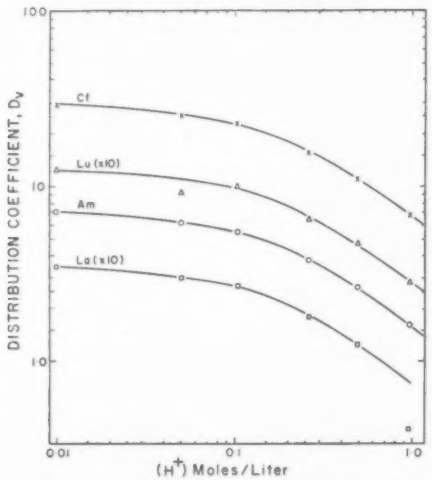

FIG. 5.—Dependence of distribution coefficients on acidity at constant chloride ion concentration. Total chloride ion was nominally 10·15 M using solutions B, C, A, D, E, and F (Table 1) at flow-rates of 0·26–0·55 ml/cm² min. Resin bed = 6 mm diam × 11·2 cm, Dowex-1, 8% DVB.

in view of the lower adsorption of metal ions from HCl solutions when compared to LiCl solutions,[5] and because of the uniform behaviour of the four elements used in this study, further interpretations would appear to lie in the properties of concentrated electrolytes rather than of individual complex metal anions. Several possible explanations have been proposed. One given by KRAUS and NELSON[16] ascribes weak acid properties to all of the complex anions investigated, thereby leading to the formation of non-adsorbable neutral species. Another, advanced by CHU and DIAMOND[17], suggests a salting of the tracer anion into the solution phase caused by a high concentration of undissociated HCl within the resin bead. Due to a lesser degree of association the same effect would not occur with LiCl. HORNE *et al.*[18,19,20] attribute the generally observed effect to ion-pairing between the anion metal complexes and the cation of the supporting electrolyte in the low dielectric constant medium of the resin whenever the dielectric constant of the external solution is high. Without substantial evidence to favour one of these hypotheses, further investigations of this type of effect seem warranted.

[16] K. A. KRAUS and F. NELSON, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva*, 1955, **7**, 113. United Nations (1955).
[17] B. CHU and R. M. DIAMOND, *J. Phys. Chem.* **63**, 2021 (1959).
[18] R. A. HORNE, *J. Phys. Chem.* **61**, 1651 (1957).
[19] R. A. HORNE, R. H. HOLM and M. D. MEYERS, *J. Phys. Chem.* **61**, 1655 (1957).
[20] R. A. HORNE, *J. Phys. Chem.* **62**, 873 (1958).

The influence of the LiCl concentration upon D_v was determined by a series of column elutions with different concentrations of LiCl of constant acidity. The results are shown in Fig. 6 where ln D_v has been plotted against chloride ion concentration. Further analysis of the data with a plot of ln D_v vs. log a_{Cl^-} (not shown), where a_{Cl^-} is the chloride ion activity in the LiCl solutions, gave an approximate third order and positive dependence on a_{Cl^-} for D_v of Am and Cf. The adsorption of Lu and particularly Am and Cf ions were highly dependent on the LiCl concentration. For practical

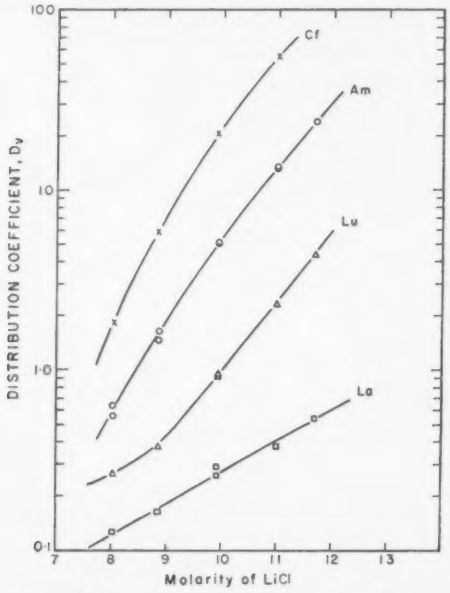

FIG. 6.—Distribution coefficients of americium, californium, lanthanum and lutecium as a function of LiCl concentration. Resin bed = 6 mm diam × 10·9 cm, Dowex-1, 8% DVB. Solutions G, H, A, I, and J (Table 1) nominally 0·1 M HCl were used at flow-rates of 0·25–0·54 ml/cm² min.

use superior actinide-lanthanide group separations are found in the region around 10 M LiCl. Below 8 M LiCl the two series of elements tend to merge, and above 10 M the elution time becomes inconveniently long.

D. *Elution order of the actinides and lanthanides*

Reliable ratios of D_v were obtained by determining, in a single elution, the elution positions of as many rare earths and tripositive actinides as were available. In one experiment fourteen rare earths (no Pm) and ^{241}Am, ^{244}Cm, ^{249}Bk, $^{250-252}$Cf and ^{253}Es were transferred to the top of the resin bed in 100 μl of slightly acidified 10 M LiCl. The resin bed (1 cm × 12 cm) was Dowex-1, 8% DVB with a settling rate of 8–15 mm/min in water. The elution was carried out at 87°C with LiCl solution A (Table 1) at a flow rate of 0·27 ml/cm² min. For analytical purposes the size of the rare earth fractions collected was 10 per cent of that of the transuranics with each transuranic fraction representing 0·205 bed volumes.

The elution order of the actinides and the band position of the lanthanides obtained in this experiment are shown in the elution curve of Fig. 7. The dashed curve for

Pu(III) ions was taken from a separate elution of Pu and Am, and after normalization to Am, was inserted to show the relative elution position of plutonium. To maintain plutonium in the tripositive valence state a solution containing 1 g of $Na_2S_2O_5$ per 100 ml of LiCl solution was used. Similar concentrations of NH_2OH, N_2H_4, or iodide ion did not prevent the oxidation of Pu(III) by trace amounts of free chlorine.

Fig. 7 illustrates the possibilities of isolating individual or small groups of transplutonium elements in addition to a group separation from the lanthanides. As an

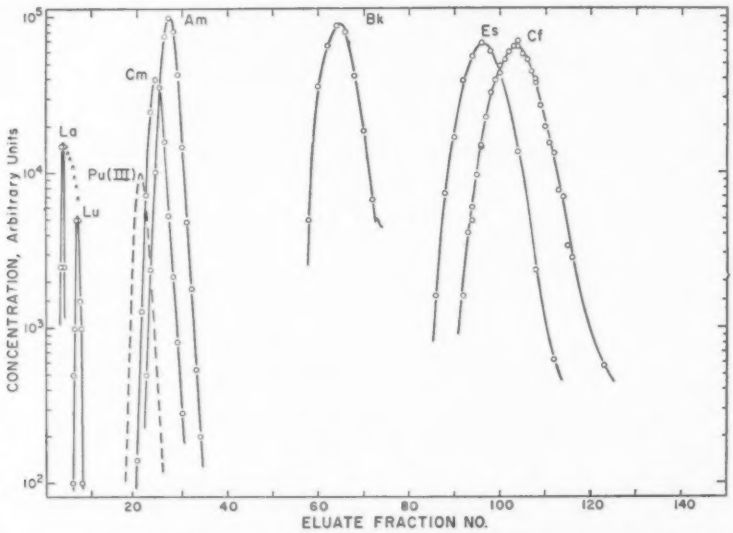

FIG. 7.—Elution of lanthanides and tripositive actinides from Dowex-1, 8% DVB at 87°C using 10 M LiCl (solution A, Table 1) at a flow-rate of 0·27 ml/cm² min. Resin bed = 1 cm diam × 12 cm.

example, the transcurium fraction from the long term neutron irradiation of a transuranic target can be separated from the major mass of Pu, Am, Cm and rare earth fission products by using in sequence 10 M LiCl, 10 M HCl and 1 M HCl eluants. The transcurium fraction is readily removed from the resin bed with 10 M HCl[2] after completion of the elution of Am and Cm ions with 10 M LiCl. Plutonium, if pre-oxidized with a small amount of NH_4NO_2, has been conveniently separated free of the other actinides during the same column operation, as plutonium (>III) is very strongly adsorbed from 10 M LiCl or 10 M HCl by Dowex-1 resin; hence, of the above eluants it is removed from the resin bed only with 1 M HCl.

In Fig. 8 the elution sequence of the actinides and lanthanides with LiCl (solid lines) is compared to the sequence using NH_4SCN.[15] It is to be noted that the actinides and lanthanides experienced the same effect in both media, since, except for plutonium, a complete correlation in elution order is observed. Moreover, the actinides reproduced the elution order of their corresponding lanthanide homologues, although larger separation factors occurred within the actinide series. It is clear that the elution order does not follow the progressive order of the ionic radii in either series (that is, a monotonic function of the atomic number).

The *f* orbital hybridization theory[4] does not seem adequate to explain[21] these corresponding "reversal" effects within *both* series of elements, inasmuch as (and probably correctly) partial covalent bonding is at the same time used to account for the actinides undergoing greater chloride complex formation than the lanthanides. Essentially the same doubts, based on similar disorders found in the elution positions of certain lanthanides and actinides from cation exchange resin with various concentrations of HCl, have also been expressed by CHOPPIN.[22] In some instances he

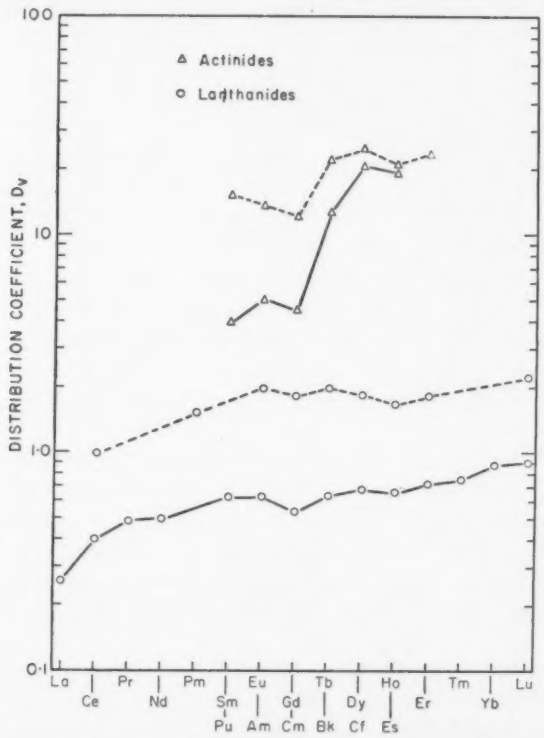

FIG. 8.—Summary of the elution order of the actinides and lanthanides from Dowex-1 resin as a function of atomic number.
—— Elutions with 10 M LiCl from Dowex-1, 8% DVB at 87°C.
- - - - Elutions with 2 M NH_4SCN from Dowex-1, 8% DVB at 33°C; D_v calculated from data of ref. 15.

found that "reversals" were sensitive to the particular type of cation exchange resin used. Additional evidence for other interpretations is the recently reported temperature-dependence of the order of adsorption of La and Eu ions by Dowex-50, 12% DVB from dilute $HClO_4$.[23]

Anion exchange behaviour of the lanthanides, using $LiNO_3$ eluant, is unusual in that the elution order of the series is reversed from that found in other media including LiCl solutions.[24] At constant molarity $LiNO_3$ the adsorption of the lanthanides

[21] J. J. KATZ and G. T. SEABORG, The Chemistry of the Actinide Elements p. 468. Methuen, London (1957).
[22] G. R. CHOPPIN, *The XVII International Conference for Pure and Applied Chemistry*, Abstract A301, Munich (1959).
[23] K. A. KRAUS and R. J. RARIDON, *J. Phys. Chem.* **63**, 1901 (1959).
[24] Y. MARCUS and F. NELSON, *J. Phys. Chem.* **63**, 77 (1959).

decreases with increasing atomic number. Ion-exchange resins are generally assumed to have little selectivity toward the complex rare earth ions of the same type and charge. The elution order is then determined primarily by the complexing tendencies of the inorganic anion for the metal ions. From ionic radii considerations alone, a reversed elution order would be expected only if, due to some special properties, the nitrate ions formed complex aggregates with the *hydrated* lanthanide ions. Conversely, assuming that anionic chloride complexes were adsorbed by the resin from LiCl solutions, the elution order of the lanthanides indicates that chloride ions are located *inside* the hydration sphere.

E. *General discussion*

It was found that by increasing temperature, resin cross-linkage, and LiCl concentration, the selectivity and adsorption were improved while an increase of HCl concentration caused a decrease in adsorption. Excellent actinide–lanthanide separations, as well as separations of individual or two-membered groups of the transplutonium elements, were achieved at 87°C with Dowex-1, 8% DVB (8–15 mm/min settling rate in water) using 10 M LiCl acidified to 0·1 M H^+ at flow rates of 0·3–0·6 ml/cm^2 min. Under certain circumstances it may be desirable to use conditions that depart from those given above. In such cases, data obtained in this study and the application of the theoretical equations derived by GLUECKAUF[8,25] for the operation of ion-exchange columns enable one to determine the optimum conditions required.*

Column operations when applied to rare earth fission product separations have been carried out in heavily shielded facilities by remote control. Under these conditions and particularly with greater than 100 mg quantities of ^{242}Cm, the elutions cannot be controlled as precisely as in the laboratory. For these reasons the decontamination from rare earth fission products has been less than optimum. Nevertheless, the use of LiCl solutions rather than the alternatives, NH_4SCN or concentrated HCl, is advantageous. In comparison to concentrated HCl, LiCl solutions are handled with less corrosion in remote control systems. Ammonium thiocyanate readily polymerizes[26] in acid solutions and reacts in an explosive exothermic manner with H_2O_2 formed in the degradation of aqueous solutions by high concentrations of α-emitters.[27]

* Diffusion coefficients encountered in the theoretical expressions can be calculated from elution data and resin particle sizes using equations (14) and (25) of reference 25.

[25] E. GLUECKAUF, *Ion Exchange and its Applications*, pp. 34–45. Society of Chemical Industry, London (1955).
[26] W. LATIMER and J. HILDEBRAND, *Reference Book of Inorganic Chemistry*, Revised Edition, p. 286. Macmillan, New York (1940).
[27] W. W. T. CRANE. Private communication (1956).

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 361 to 365. Pergamon Press Ltd. Printed in Northern Ireland

EXTRACTION AND ION EXCHANGE INVESTIGATION OF URANIUM(VI) CHELATES

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(*Received* 21 *July* 1960; *in revised form* 13 *October* 1960)

Abstract—The composition and the stability constants of uranium(VI) chelates with nitrilotriacetic acid, ethylenediaminetetraacetic acid and 1,2-diaminecyclohexanetetraacetic acid have been determined by means of extraction and ion exchange methods.

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DURING recent years aminopolycarboxylic acids have become increasingly important chelating agents. Although investigations concerning the interaction of these agents with many metal ions have been described,[1] no data concerning uranium(VI) ion complexing with these aminopolycarboxylic acids have been reported. The chelates of uranium(VI) with nitrilotriacetic acid (H_3X), ethylenediaminetetraacetic acid (H_4Y) and 1,2-diaminecyclohexanetetraacetic acid (H_4Z) are not soluble in organic solvents of low dielectric constants and therefore the composition and the stability constants were determined by means of the extraction method, previously described.[2] These constants have been verified by ion exchange method.[3]

EXPERIMENTAL

Materials. All reagents used were of A.R. purity; the organic solvents were purified by distillation. The sodium form of the cation exchanger Dowex 50 with 8% DVB, particle size of 20–50 mesh, was used. The exchange capacity was about 3·75 mequiv/g of air-dried hydrogen form of the exchanger.

Procedure. The determinations of pH were made with a Radiometer PHM4b using a glass electrode with a saturated calomel electrode as a reference electrode. Spectrophotometric measurements were carried out on a Zeiss universal spectrophotometer.

Distribution measurements. Equal volumes (5 ml) of a 0·1 M solution of benzoylacetone in benzene and 0·1 M solution of $NaClO_4$ containing uranium(VI) and corresponding amounts of aminopolycarboxylic acid were shaken for 60 min. The pH was adjusted by addition of small amount of NaOH or $HClO_4$. After the separation of the two phases, the equilibrium concentration of uranium(VI) in the organic phase was determined spectrophotometrically at 390 mμ.[4] The distribution ratio between organic and aqueous phase could be calculated from the equation

$$q = \frac{c_{org}}{c_{tot} - c_{org}}$$

where c_{org} is the equilibrium concentration of uranium(VI) in organic phase,

c_{tot} is the total concentration of uranium(VI); in all experiments c_{tot} was 10^{-4} M.

Ion exchange measurements. Twenty millilitres of 0·1 M $NaClO_4$ containing uranium (VI) and aminopolycarboxylic acid were shaken with 0·200 g of ion exchanger for 4 hr. The equilibrium concentration of uranium(VI) in aqueous phase was determined spectrophotometrically in the form of

[1] J. BJERRUM, G. SCHWARZENBACH and L. G. SILLÉN, *Stability Constants of Metal Ion Complexes*, Chemical Society, London. (1957)
[2] J. STARÝ, *Coll. Czech. Chem. Comm.* **25**, 2630 (1960).
[3] J. SCHUBERT, *J. Phys. Colloid. Chem.* **52**, 340, 352 (1948).
[4] J. STARÝ, *Coll. Czech. Chem. Comm.* **25**, 890 (1960).

the chelate with dibenzoylmethane[5,6] at 403 mμ. The distribution ratio between the resin and aqueous phase was calculated from the equation

$$\varphi = \frac{c_{tot} - c_{aq}}{c_{aq}} \frac{v}{m}$$

where c_{tot} is the total concentration of uranium(VI), $2{\cdot}5 \cdot 10^{-5}$ and $5{\cdot}0 \cdot 10^{-5}$ M,
c_{aq} is the equilibrium concentration of uranium(VI) in aqueous phase,
v is the total volume of solution in millilitres
m is the weight of air dried ion exchanger in grammes.
All distribution measurements were carried out at room temperature (20 ± 1°C).

Method of calculation. The composition and stability constants were determined from the general equation:[2]

$$\frac{q_0}{q} - 1 = \sum_{s=1} \sum_{t=0} K'_{s,t} [B]^s [OH]^t \qquad (1)$$

where q_0, q are the distribution ratios in the absence of or in the presence of aminopolycarboxylic acid, respectively, $K'_{s,t}$ is the stability constant of complex $UO_2B_s(OH)_t$, where B is the anion of the aminopolycarboxylic acid.

The values of q_0 for distribution of uranium(VI) between a 0·1 M solution of benzoylacetone in benzene and a 0·1 M solution of $NaClO_4$ were calculated from the relation:[4]

$$q_0 = 2{\cdot}1 \cdot 10^{-8} [H^+]^{-2} \qquad (2)$$

The equilibrium concentration of B was calculated from the total concentration of aminopolycarboxylic acid, the dissociation constants of this acid and the equilibrium pH. The part of aminopolycarboxylic acid bound with uranium(VI) was taken into account. The hydroxocomplexes are not formed, if the values $(q_0/q - 1)$ for all pH depend only on $[B]$.[2] Then

$$\frac{q_0}{q} - 1 = \sum_{s=1} K'_s [B]^s \qquad (3)$$

where K'_s is the stability constant of the complex UO_2B_s. The stability constants of the complex UO_2B_s determined by the ion exchange method were calculated in a similar way from the equation[3]

$$\frac{\varphi_0}{\varphi} - 1 = \sum_{s=1} K'_s [B]^s \qquad (4)$$

where φ_0 φ are the distribution ratios of uranium(VI) between the resin phase and the aqueous phase in the absence or in the presence of aminopolycarboxylic acid, respectively. The mean value from 10 measurements of φ_0 at pH 4–5 was 2700.

RESULTS AND DISCUSSION

The uranium(VI) *complexes with nitrilotriacetic acid* (H_3X). The distribution ratios of uranium(VI), q, as a function of pH for various concentrations of H_3X are presented in Fig. 1. The broken line shows the dependence of q_0 on pH.[4] For any value of q the corresponding value of q_0 has been calculated. If the values of log $[(q_0/q) - 1]$ for all pH are plotted against $-\log [X^{3-}]$, they fit rather well to a straight line with a slope 1·0/. This means that only the complex of the type UO_2X^- is formed. The stability constant of UO_2X^- calculated from equation (3) is $(3{\cdot}6 \pm 0{\cdot}3) \cdot 10^9$, from 30 measurements. This value was verified by the ion exchange method. The mean value of the stability constant, from 15 measurements, calculated from equation (4) is $(2{\cdot}2 \pm 0{\cdot}2) \times 10^9$. The concentration of nitrilotriacetic acid was $1{\cdot}0 \times 10^{-3}$M and $2{\cdot}0 \times 10^{-3}$ M and the pH was 4·0–5·0.

[5] V. MOUČKA and J. STARÝ, *Coll. Czech. Chem. Commun.* In press.
[6] R. PŘIBIL and M. JELÍNEK, *Chem. Listy* **47**, 1326 (1953); *Coll. Czech. Chem. Comm.* **19**, 613 (1954).

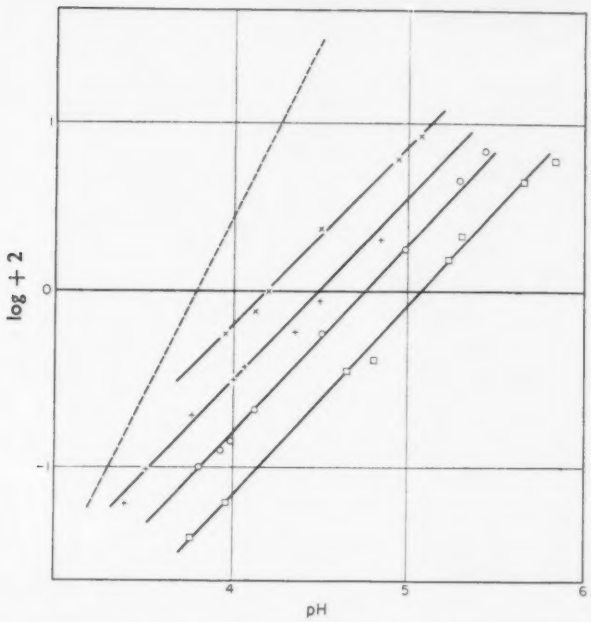

FIG. 1.—The extraction of uranium(VI) by a 0·1 M solution of benzoylacetone in the presence of various concentrations of nitrilotriacetic acid; × 0·0005 M, + 0·0010 M, ○ 0·0020 M, □ 0·0040 M.

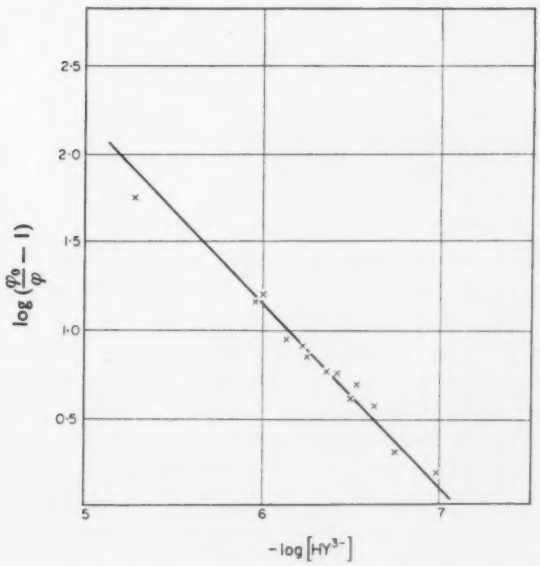

FIG. 2.—Log $\left(\frac{\varphi_0}{\varphi} - 1\right)$ values vs. $-\log [HY^{3-}]$ for 0·0005 M ethylenediaminetetraacetic acid. (slope 1·0)

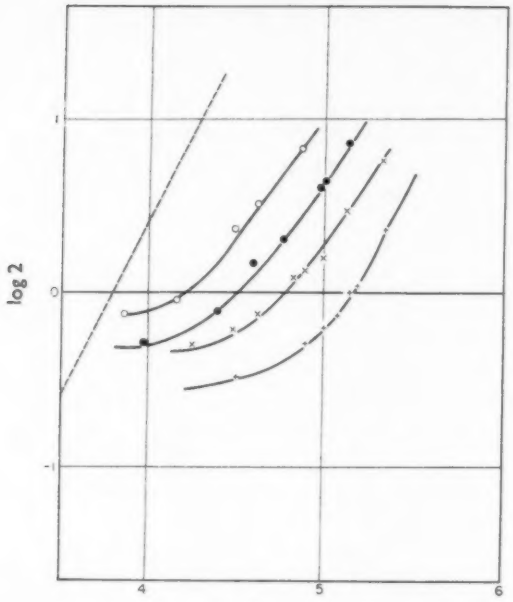

FIG. 3.—Extraction of uranium(VI) by a 0·1 M solution of benzoylacetone in the presence of various concentration of 1,2 diaminecyclohexanetetraacetic acid; ○ 0·0020 M, ● 0·0050 M, × 0·0100 M, + 0·0200 M.

TABLE 1.—LOG K′ VALUES FOR URANIUM(VI) COMPLEXES WITH NITRILOTRIACETIC ACID (H_3X), ETHYLENEDIAMINETETRAACETIC ACID (H_4Y) AND 1,2-DIAMINECYCLOHEXANETETRAACETIC ACID (H_4Z)

Reaction	log K′	
	extraction	ion exchange
$UO_2^{2+} + X^{3-} \rightleftarrows UO_2X^-$	9·56 ± 0·03	9·41 ± 0·04
$UO_2^{2+} + HY^{3-} \rightleftarrows UO_2HY^-$	7·32 ± 0·02	7·13 ± 0·04
$UO_2^{2+} + HZ^{3-} \rightleftarrows UO_2HZ^-$	5·27 ± 0·03	5·27 ± 0·03

The uranium(VI) *complexes with ethylenediaminetetraacetic acid* (H_4Y). The formation of uranium(VI) complexes with H_4Y was investigated by the extraction method in a previous paper.[2] It was found, that in the pH range of about 4–7, uranium(VI) forms with H_4Y a complex of the type UO_2HY^-. The stability constant of this complex was found to be $(2{\cdot}1 \pm 0{\cdot}1) \times 10^7$. KLYGIN *et al.*[7] reported recently the formation of this complex and estimated the magnitude of the stability constant to be $3{\cdot}6 \times 10^5$. This value seems too low and we have therefore redetermined the stability constant of the uranium(VI) complex with H_4Y by the ion exchange method. The log $[(\varphi_0/\varphi) - 1]$ values for all pH (3·5–5·0) are plotted against $-\log (HY^{3-})$ in Fig. 2. The mean value from 13 measurements of the stability constant calculated from equation (4), $K'_{UO_2HY^-} = (1{\cdot}35 \pm 0{\cdot}12) \times 10^7$, is in good agreement with the value determined by the extraction procedure.

[7] A. E. KLYGIN, I. D. SMIRNOVA and N. A. NIKOLSKAJA, *Russian J. Inorg. Chem.* **4**, 2623 (1959).

The uranium(VI) *complex with* 1,2-*diaminecyclohexanetetraacetic acid* (H_4Z). In Fig. 3 the distribution ratios of uranium(VI) for various concentration of H_4Z and H^+ are presented. The values of log $[(q_0/q) - 1]$ for all pH values plotted against $-\log (HZ^-)$ give an approximatively straight line of the slope 1·0. This results shows clearly the formation of the complex UO_2HZ^-. The mean value from 24 measurements of the stability constant calculated from equation (3) is $(1{\cdot}85 \pm 0{\cdot}15) \times 10^5$. The same mean value from 23 measurement, i.e. $(1{\cdot}85 \pm 0{\cdot}15) \times 10^5$ is obtained from ion exchange data. The concentration of H_4Z was 0·0020 M and 0·0050 M, and the pH was 4–5.

The results of this investigation are listed in Table 1. Uranium(VI) forms with H_3X the complex of the type UO_2X^-, while with H_4Y and H_4Z it forms the hydrogen containing complexes UO_2HY^- and UO_2HZ^-, respectively. The stability constants determined by two independent methods are in exceptionally good agreement. It is very interesting to note that contrary to the behaviour of all other metal ions,[1] a much more stable uranium(VI) complex is formed with H_4Y than with H_4Z. From the above described results, it follows that the use of H_4Z as a masking agent for the separation of uranium(VI) from many metal ions is more advantageous than the more usual use of H_4Y.

Acknowledgements—The authors wish to thank Professor F. Běhounek and Docent D.Sc. V. Majer for their interest in this work and Mrs. V. Urbanova for her technical assistance.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 366 to 372. Pergamon Press Ltd. Printed in Northern Ireland

THE CO-CRYSTALLIZATION OF ULTRAMICRO QUANTITIES OF ALKALI METALS WITH AMMONIUM DIPICRYLAMINATE

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(*Received* 25 *July* 1960)

Abstract—The co-crystallization of ultramicro quantities of alkali metals with ammonium dipicrylaminate was investigated. Radiotracer techniques were employed to measure the quantitative removal of these elements. Conditions were developed for the separation of potassium, rubidium and cesium as a group by this process; sodium remained largely associated with the mother liquor.

THE isolation of ultramicro quantities of elements from solution by co-crystallization with an organic compound has been described.[4] This process is based upon FAJANS Rule[1] which predicts that a crystallized organic reagent is enriched with trace element if the trace element and the organic reagent combine to form a compound whose insolubility is greater than that of the reagent alone.

The properties of the alkali metal–dipicrylamine system provide the opportunity to further verify the applicability of Fajans Rule in the selection of an organic compound for the isolation of minute quantities of an element from solution by co-crystallization. The potassium, rubidium and cesium salts of dipicrylamine are more insoluble than ammonium dipicrylaminate, while the sodium salt is more soluble; moreover, the degree of insolubility increases with increase in the molecular weight of the alkali metal dipicrylaminate.[3]

The use of dipicrylamine in the separation of small quantities of alkali metals from solution has received some attention. Cesium was effectively separated from fission products in carrier free form by the co-precipitation with thallium dipicrylaminate.[5] The general aspects of the co-precipitation of small but weighable quantities of cesium with sparingly soluble dipicrylaminates was also investigated.[2]

The current study examines the co-crystallization of trace quantities of sodium potassium rubidium and cesium with ammonium dipicrylaminate. The experimental method involved the co-crystallization of an element of the alkali metal group with dipicrylamine upon crystallization of fractions of carrier from solution with ammonium chloride. The influence of reagent concentrations as well as other variables upon the distribution of trace element between solution and solid phase was evaluated. To provide for the accurate measurement of ultramicro quantities of the alkali metals appropriate radioactive tracers were used.

[1] K. FAJANS and P. BERR, *Ber. Dtsch. Chem. Ges.* **46**, 3486 (1913).
[2] I. M. KORENMAN and G. A. SHATALINA, *J. Analyt. Chem. U.S.S.R.* **7**, 335 (1952).
[3] V. KOURIM and J. KRTIL, *The Proceedings of the Second International Conference on Peaceful Uses of Atomic Energy, Geneva* 1958, Vol. 28, p. 139. United Nations (1958).
[4] H. V. WEISS and M. G. LAI, *Analyt. Chem.* **32**, 475 (1960).
[5] N. YAMAGATA and S. WATANABE *Bull. Chem. Soc. Japan*, **30**, 580 (1957).

EXPERIMENTAL

Reagents

Dipicrylamine solution. A weighed quantity of dipicrylamine (Eastman Organic Chemicals) was dissolved in 0·6 N NaOH, the pH was adjusted to 7·5 with dilute hydrochloric acid and this solution was diluted to a desired volume.

Ammonium chloride, reagent grade. This solution was prepared to contain 48·8 mg/ml. Buffer pH 7:3·53 parts of 0·1 M citric acid mixed with 16·47 parts of 0·2 M dibasic sodium phosphate.

TABLE 1.—OPTICAL DENSITY AT 432 mμ OF DIFFERENT CONCENTRATIONS OF DIPICRYLAMINE DISSOLVED IN pH 7·0 BUFFER

Dipicrylamine (μg/ml)	Optical density
5·5	0·342
11·0	0·675
17·6	1·071
22.0	1·340

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Tracers and their measurement

The alkali metal tracers were procured from Oak Ridge National Laboratory or Nuclear Science and Engineering Corporation. Sodium-22 and cesium-137 were carrier-free while the specific activity of potassium-42 and rubidium-86 was 467 and 12,563 mc/g, respectively. The maximum quantity of inert carrier used in an experiment was limited to 10^{-8} g/ml and usually less than this quantity was introduced.

Other radionuclides studied were obtained from a variety of sources. Not all were carrier free, however the same limitation on carrier concentration was observed. The purity of these tracers was established by γ-ray pulse height analysis.

These radionuclides were measured in a γ-ray well scintillation counter. The distribution of the radioelement was determined by measuring the activity of the crystalline phase. The isolated crystals were dissolved in acetone diluted to a definite volume and compared with a radioactive standard of the same volume.

Spectrophotometric determination of dipicrylamine

To evaluate the influence of variables upon the crystallization of dipicryalamine a spectrophotometric method was developed for its determination. With a Beckman spectrophotometer the maximum spectral absorption occurred at 432 mμ when dipicrylamine was dissolved in the pH 7 buffer. The optical density at this wavelength of 5·5–22·0 μg of dipicrylamine per ml of buffer is shown in Table 1. The relation between reagent concentration and optical density adhered to Beer's Law.

The dipicrylamine distribution was usually determined by assay of the liquid phase. After crystallization, the crystals were removed by filtration and the filtrate was diluted to some definite volume. An appropriate aliquot was removed and diluted to volume with buffer solution. The concentration of dipicrylamine in this solution was determined by comparing its optical density with a standard graph derived from the data of Table 1.

To ensure that analysis of the dipicrylamine concentration in the aqueous phase was accurate, experiments were performed in which both the solid and liquid phases were analysed . To analyse the solid phase the crystals were first dissolved in acetone and then diluted to a desired volume with buffer solution. Analyses of the separate phases completely accounted for the total quantity of dipicrylamine used and the method was considered reliable.

Experimental method

To 20 ml of dipicrylamine solution was added 1 ml of a solution of radioactivity which contained about 10^4 counts/min. A quantity of ammonium chloride solution was added and the final volume

was adjusted to 24 ml. Unless otherwise noted, in the resultant homogeneous solution the concentration of dipicrylamine and ammonium chloride was 9·5 and 19·0 mM respectively. This solution was allowed to crystallize at 5°C for 20 hr except for the series in which the effect of temperature and crystallization time were under examination. Crystallized material was separated from mother liquor on paper by filtration through a tower and sucked dry. The distributions of dipicrylamine and radioelement were determined as described.

RESULTS

Table 2 shows the relationship between crystallization time and recovery of both the reagent and co-crystallized cesium. The recovery of dipicrylamine increased

Table 2.—Effect of crystallization time upon the recovery of dipicrylamine and cesium

Crystallization time (hr)	Dipicrylamine crystallized (%)	Cesium recovered (%)
7	57·7	79·1
24	93·3	100·0
53	96·6	100·1
77	98·5	100·1

Table 3.—Effect of pH upon the recovery of dipicrylamine and cesium

pH	Dipicrylamine crystallized (%)	Cesium recovered (%)
6·3	91·2	99·9
7·4	91·3	99·6
8·0	93·0	101·2
9·0	91·6	100·8
10·0	91·9	99·5
11·0	89·2	99·7

progressively over the observation period 7–77 hr. On the other hand after only 24 hr the recovery of cesium was already quantitative.

To determine the effect of pH upon the recovery of cesium and organic carrier, the hydrogen ion concentration of the dipicrylamine solution was first adjusted with either hydrochloric acid or sodium hydroxide and the crystallizing agent was then added. The recovery of either component was essentially unaffected by pH in the range 6·3–11·0 (Table 3). More acid pH values were not evaluated since homogeneity of solution prior to crystallization with ammonium chloride was unobtainable at greater hydrogen ion concentration.

Table 4 shows the effect of dipicrylamine and ammonium chloride concentration as well as temperature upon the co-crystallization of cesium and the recovery of dipicrylamine. The quantity of dipicrylamine which crystallized increased as the ammonium chloride concentration was raised. On the other hand the co-crystallized cesium assumed a different pattern. The recovery of cesium reached a maximum

value at an optimum concentration of crystallizing agent and the crystallized dipicrylamine was enriched with microcomponent. The point at which this maximum occurred with reference to the ammonium chloride–dipicrylamine molar ratio was dependent upon the initial concentration of dipicrylamine in solution. Further, the co-crystallization of cesium was enhanced in more concentrated dipicrylamine solutions. As the ammonium chloride–dipicrylamine molar ratio was raised beyond the optimum, the crystalline dipicrylamine carried less cesium.

TABLE 4.—THE RECOVERY OF DIPICRYLAMINE AND CESIUM FROM SOLUTION AT DIFFERENT CARRIER REAGENT AND CRYSTALLIZING AGENT CONCENTRATIONS AND AT DIFFERENT TEMPERATURES

Ammonium chloride dipicrylamine molar ratio	Dipicrylamine crystallized (%)				Cesium recovered (%)			
	Dipicrylamine (mM)				Dipicrylamine (mM)			
	4·8	7·1	9·5		4·8	7·1	9·5	
	Temperature (°C)				Temperature (°C)			
	5	5	22	5	5	5	22	5
1·0	1·4	18·5	10·0	19·0	1·1	19·1	17·4	19·0
1·5	—	—	63·4	83·6	—	—	95·0	100·1
2·0	13·4	86·7	74·5	91·3	31·2	99·2	98·7	99·6
2·5	—	—	83·9	93·5	—	—	100·1	99·8
3·0	—	—	88·5	95·8	—	—	99·7	99·7
4·0	—	—	92·6	96·6	—	—	96·0	97·2
6·0	60·4	96·5	95·5	98·3	78·2	87·9	95·4	88·4
10·0	85·1	98·8	97·5	99·0	93·9	83·9	74·0	82·7
16·0	94·0	—	—	—	77·9	—	—	—
20·0	95·8	—	—	—	68·0	—	—	—

A greater quantity of organic reagent crystallized from solution at the lower temperature and the amount of cesium which it carried was comparably greater.

The recovery of the other alkali metals by co-crystallization with dipicrylamine in which the effect of different ammonium chloride-dipicrylamine molar ratios were evaluated is shown in Fig. 1. Results obtained with cesium are included for comparison. With the exception of sodium, the recovery of the other alkali metals followed the same pattern described for cesium. The quantity of co-crystallized microcomponent reached a maximum and then diminished as the crystallizing agent concentration was elevated. The degree of co-crystallization at the maximum was greater the heavier the atomic weight of the element. This relationship, however, was reversed for rubidium and cesium at the higher ammonium chloride concentrations in which derichment of microcomponent was manifest.

Sodium co-crystallized only minimally and was not enriched in the solid phase. Unlike the other alkali metals, the recovery of this element increased progressively as the concentration of ammonium chloride was raised.

The co-crystallization of other radioelements with dipicrylamine is shown in Table 5. Recovery values ranged from 1·7 to 50·5 per cent.

DISCUSSION

The conditions for the co-crystallization of minute quantities of alkali metals with dipicrylamine are defined primarily by the dipicrylamine concentrations and the molar ratio between ammonium chloride and dipicrylamine. The recovery of alkali

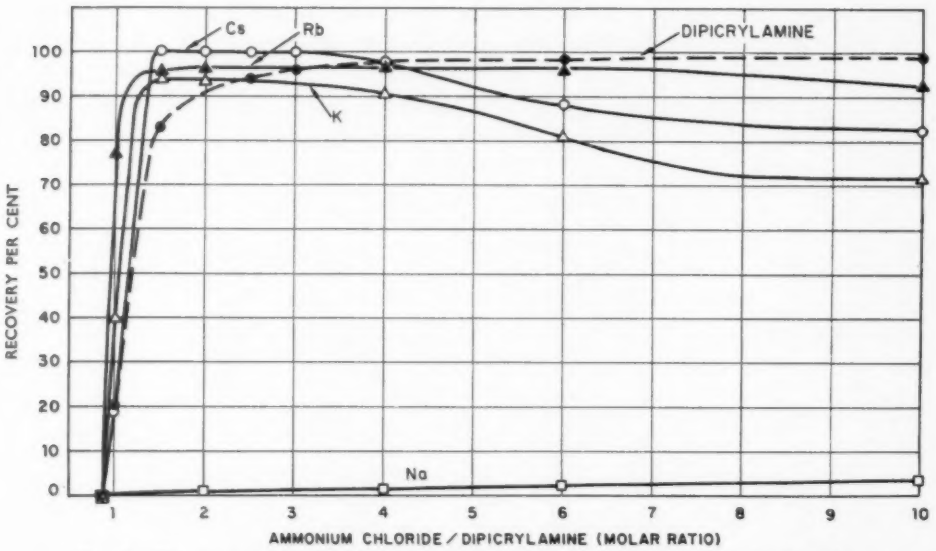

Fig. 1.—The co-crystallization of trace quantities of alkali metals with dipicrylamine using ammonium chloride as crystallizing agent.

Table 5.—The cocrystallization of diverse elements with ammonium dipicrylaminate

Radioelement	Recovery (%)
Ce-144	50·5
Fe-59	48·7
Ru-106	38.1
Zn-65	23·5
Zr-95	20·0
Sb-125	14·4
Co-60	3.3
Mo-99	2·3
Mn-54	1·7
Ba-133	1·7

metal attains a maximum value as the ammonium chloride–dipicrylamine molar ratio is raised to a certain level depending upon the concentration of dipicrylamine in solution. However, as the ammonium chloride–dipicrylamine molar ratio is raised even higher the recovery of alkali metal is diminished despite enhanced recovery of the organic carrier. Clearly the ammonium ion competes with the alkali metal for

combination with dipicrylamine. This type of competition was previously observed in a study of the co-crystallization of the alkaline earth metals with potassium rhodizonate when this same salt was used as the crystallizing agent.[4]

Despite the competitive aspects of the crystallizing system quantitative or very nearly quantitative recovery of potassium, rubidium and cesium from very dilute solution can be achieved. In fact the inhibitory effect of ammonium chloride can be minimized if the dipicrylamine solution is at the limit of its solubility. Under such circumstance a smaller quantity of ammonium chloride is required to crystallize a definite amount of dipicrylamine from solution. Concomitantly, the competitive

TABLE 6.—EFFECT OF CESIUM CARRIER UPON THE CO-CRYSTALLIZATION OF CESIUM WITH AMMONIUM DIPICRYLAMINATE

Cesium carrier added (g/24 ml of sample)	Cesium recovery (%)
1×10^{-10}	82·6
1×10^{-7}	83·7
1×10^{-4}	87·0

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effect of ammonium ion is reduced and this situation affords more efficient co-crystallization.

Sodium dipicrylaminate is more soluble than the ammonium salt and is largely found in the mother liquor after crystallization. Interestingly, however, a small but perceptible increase of this element in the solid phase is favoured as more and more of the crystallizing agent is added. The reason for this deviation from the normal pattern is obscure.

Another anomaly is represented by the relative effect of the higher concentrations of ammonium chloride upon the co-crystallization of cesium and rubidium. The sensitivity of cesium to the inhibitory action of the crystallizing agent is such that its recovery is depressed below that of rubidium in the higher salt media. This result is not attributable to the effect of differences in inert carrier content of the tracer solutions. A series of experiments was performed in which cesium was co-crystallized from solutions which contained up to 10^{-4} g of cesium carrier per sample. Under this condition the recovery of cesium was shifted upward (Table 6). However, the shift was still not of sufficient magnitude to overcome this reversal in the recovery pattern, despite the fact that the carrier used was much in excess of the carrier introduced by way of the tracer solution in the rubidium series.

Notwithstanding this anomaly, the recovery of alkali metals under optimum conditions follows the order predicted by Fajans Rule and again points to its applicability in the choice of an organic reagent for the purpose of co-crystallizing an element from very dilute solution.

The data suggest that the enhanced recovery of microcomponent at lower temperature is associated with depression in solubility of dipicrylamine rather than an inherent effect upon the distribution of trace element between the phases.

Small to moderate amounts of other elements also co-crystallize with dipicrylamine; therefore, isolation of an alkali metal by this procedure affords only partial purification from other elements. Nor is the process effective in the separation of one alkali metal from another, except for the separation of the heavier alkali elements from sodium. Rather, co-crystallization finds its greatest usefulness as a concentrating mechanism by a method which is both simple and efficient without the mediation of an inorganic carrier.

J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 373 to 381. Pergamon Press Ltd. Printed in Northern Ireland

THE ADSORPTION OF CALCIUM, STRONTIUM AND THALLIUM IONS FROM MOLTEN SALTS BY SILICA AND ALUMINA

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(*Received* 25 *July* 1960)

Abstract—The adsorption of calcium, strontium and thallium ions by silica and alumina from a zinc chloride-potassium chloride eutectic was investigated. Adsorption rates, adsorption isotherms, and adsorption column data were determined. No adsorption for any of the cations could be obtained on the silica. Calcium and strontium were found to be adsorbed by alumina, while the thallium was not adsorbed. The rate of adsorption of strontium on alumina was twice as fast as that of calcium. The calcium isotherm at 250°C was of the general form fitted by the Freundlich or Langmuir equations, while the strontium isotherm was very anomalous. The data obtained from the adsorption column indicated that it might be feasible to separate rather large amounts of calcium and strontium from molten salts by adsorption on alumina. However, no effective way was found to elute the cations from the alumina packing.

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THE processing of spent reactor fuels to recover fissionable materials and remove radioactive fission products adds greatly to the cost of atomic power. In many reactors the fuel is in the form of metal-clad rods which must be removed from the reactor and dissolved in acid before the reprocessing can begin. With the introduction of homogeneous fuels, however, a continuous separation procedure becomes possible. In general, the homogeneous fuels that have been considered the most promising are of two types, aqueous and molten. Molten fuels have the advantage of better heat transfer characteristics and lower operating pressures. The homogeneous molten fuels which have been tested are mainly metals and fused salts containing dissolved fissionable material. One example is the experimental fused-salt fast breeder in which uranium chloride and plutonium chloride are dissolved in a mixture of sodium chloride and magnesium chloride.[1] Another fuel which has received considerable attention is molten bismuth containing dissolved uranium. Considerable work has been done on purifying this fuel by liquid-liquid extraction using molten salts.[2–5]

At the present time most of the work being done on fused salt mixtures is being concentrated on fluoride salt melts because fluorine has a very low thermal neutron absorption cross section. The salts used most frequently to dissolve the fissionable material are beryllium fluoride, lithium fluoride, potassium fluoride, sodium fluoride, zirconium fluoride and rubidium fluoride. The purification of these fuels has been studied, and the most promising methods developed to date have been the fluoride volatility process and ion-exchange.[6] The ion-exchange method seems to be the

[1] J. J. BULMER, E. H. GIFT, R. J. HULL, A. M. JACOBS, S. JAVE, E. HOFFMAN, R. L. MCVEAN, R. G. OEHL and R. R. ROSSI, CF-56-8-204 (Del.) (1956).
[2] D. W. BAREIS AEDC-3877, New York (1952).
[3] D. W. BAREIS, R. H. WISWALL, JR. and W. E. WINSEHE, *Nucleonics* **12**, 16 (1954).
[4] O. E. DWYER, *Amer. Inst. Chem. Engrs. J.* **2**, 163 (1956).
[5] F. T. MILES, D. W. BAREIS, O. E. DWYER, D. H. GURINSKY, I. KAPLAN, R. J. TEITEL and C. WILLIAMS, BNL-1072, New York (1952).
[6] H. G. MACPHERSON, ORNL-2684 (1957).

best, requiring 50 per cent less fuel stock and experiencing 30 per cent less fuel burn-up. The fluoride salt mixture with the lowest melting point is a sodium fluoride–beryllium fluoride eutectic containing 57 mole per cent sodium fluoride. The melting point of this mixture is 350°C.[7]

Because of the high interest in fluoride salts they were tested for use in this project. However, the extreme toxicity of beryllium fluoride made it impractical to consider the use of this material with our facilities, and a literature search revealed that other fluoride salt eutectics have very high melting points. A typical example is a sodium fluoride-potassium fluoride mixture which melts at 710°C.[8] It was found that fluoride salts at these high temperatures are extremely corrosive and fuse with silica, alumina and silicon carbide. Also, the selection of suitable construction materials is a problem since it is difficult for even stainless steel and Monel to stand up under these conditions.

There are, however, mixtures of chloride salts that melt as low as 122°C. Also, chloride salts are generally much more soluble in water than fluoride salts, making experimental equipment easier to clean and decontaminate. It was, therefore, decided that chloride salts would be used in the initial investigation, and if the separation method proved to be feasible for chloride salts, it might later be applied to lower melting fluoride salt mixtures if a suitable packing could be found. With the fluoride salts, construction materials would be no problem if the operation could be carried out at less than 500°C, as glass and nickel have both been used in contact with molten fluoride salts at these temperatures in an inert atmosphere.

The chloride salt system chosen for this project was a mixture of potassium chloride and zinc chloride, containing 46 mole per cent potassium chloride, and melting at 228°C. This mixture was chosen for its low melting point, stability, and high solubility in water. The high water solubility is desirable so that the equipment could be easily cleaned and decontaminated.

The only work of this type reported in the literature was done by GRUEN and is recorded in *Nature*.[9] However, no quantitative data was given. The article states only that a bed of alumina was used to adsorb Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and UO_2^{2+} from a lithium nitrate-potassium nitrate mixture containing 43 mole per cent lithium nitrate. This mixture has a melting point of 132°C. The ions were removed from the bed by the same solution containing Cl^-, SO_4^{2-}, and CN^-. There is no information as to how the analytical data were obtained or as to how efficient the separation was.

The purpose of this investigation was: (1) to determine the feasibility of separating Ca^{2+}, Sr^{2+} and Tl^+ from a molten salt solution by adsorption on alumina and silica; (2) to determine the equilibrium adsorption of these cations as a function of the concentration of the solution; (3) to select suitable flow rates for the operation of an adsorption column; (4) to see if these cations could be eluted from the packed bed after adsorption.

MATERIALS, EQUIPMENT AND PROCEDURE

As already mentioned, a potassium chloride–zinc chloride eutectic containing 46 mole per cent (31·8 weight per cent) potassium chloride was used for the solvent in this work. The melts were prepared by mixing reagent grade anhydrous salts and heating them above their melting point in contact with the atmosphere. The water adsorption by the melt, if any, was not measured. The

[7] S. I. COHEN and T. N. JONES, ORNL-2278 (1957).
[8] E. P. DERGUNOV, *Akad. Nauk SSSR Dokl.* **58**, 1369 (1940); AEC-Tr-1860.
[9] D. M. GRUEN, *Nature, Lond.* **178**, 1181 (1956).

solute cations used were Ca^{2+}, Sr^{2+}, and Tl^{+} in the form of chlorides. These cations were chosen because they exist in isotopic states as long-lived β-emitters that could be used as tracers. β-emitters were chosen because they were easy to count and required fewer safety precautions than gamma emitters. The isotopes used were ^{45}Ca, ^{90}Sr and ^{204}Tl. The adsorbents used were grade F-1 commercial activated alumina and 20–30 mesh silica. The alumina, originally 8–14 mesh, was ground and sieved to 20–30 mesh material for use in this investigation.

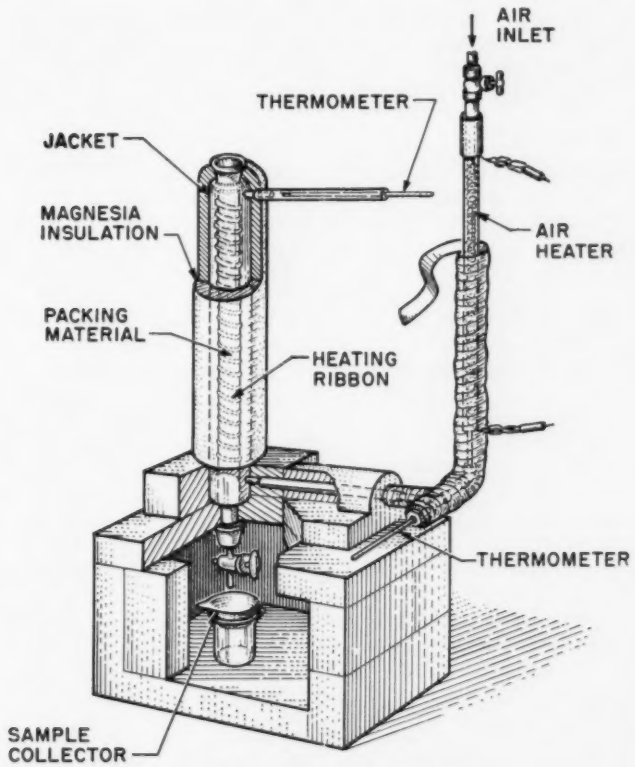

FIG. 1.—Adsorption column.

An apparatus was constructed in which the adsorption isotherms for the cations could be determined, and a chromatographic column was also constructed so that the adsorption isotherm data could be checked in a continuous flow system. The apparatus used to collect the adsorption isotherm data consisted of a 250 ml beaker surrounded by a constant temperature furnace made from 4 in. Monel pipe. A stirring device was inserted into the glass vessel and was driven by an external motor.

Fig. 1 is a diagram of the chromatographic column and accessory equipment. The 30 in. column (packed to a depth of 12–14 in.) was made from 25 mm Pyrex glass tubing. The column was jacketed so that hot air could be blown through the jacket to maintain the column at a constant temperature. A special glass stopcock was attached to the bottom of the column to control the flow of molten salt through the column. A fine mesh monel screen was placed at the bottom of the column to support the packing.

Special sample holders $\frac{1}{2}$ in. long were fabricated from brass tubing to hold the radioactive salt samples. A standard end-window proportional counting tube with reproducible geometry, and a Baird-Atomic Model 7300 counting system formed the tracer counting set-up.

Adsorption isotherms

To collect the adsorption isotherm data, solutions of known cation concentration were made up by adding known weights of cation chloride to eutectic salt mixtures. A very small amount of radioactive tracer was then added to each solution and stirred until well mixed. The initial number of counts in the solution was determined, and then a known weight of cation solution was placed in the 250 mm beaker along with a known weight of adsorbent. The solution was stirred until equilibrium was reached between the solution and adsorbent. Samples of molten salt solution were taken every 30 min. When the number of counts from three successive samples fell within the accuracy of the counter, it was assumed that equilibrium had been reached. In this procedure a basic assumption was that the ratio of the radioactive isotope adsorbed to that remaining in solution was the same as the ratio of the stable isotope adsorbed to that remaining in solution. All data were taken at 250 ± 5°C.

Adsorption column

In collecting data using the adsorption column, both frontal analysis and elution analysis were employed. In each case the runs were made with a single cation. The column was first wet with pure eutectic and the tracer solution to be tested was applied to the top of the bed. In elution analysis a small amount of tracer solution was applied to the top of the packed bed followed by pure eutectic. When frontal analysis was used, tracer solution was applied continuously to the top of the bed. The superficial velocity of the molten salt through the packed bed was obtained by measuring the rate of movement of the molten salt meniscus in the Pyrex tube above the packed bed. The actual velocity of the molten salt through the packed bed was calculated by dividing the superficial velocity by the void fraction of the bed, the latter being determined by the water displacement method. The void fraction of 0·57 found this way for the alumina packing (0·38 for silica) agreed well with that determined by visual observation of the velocity of a coloured liquid front in the packing as compared to the velocity of the meniscus above the packing. The velocity of the molten salt was kept essentially constant by allowing the level of the molten salt in the column to drop only a short distance before more molten salt was added.

In taking samples both from the column and from the adsorption isotherm apparatus, the sample holders were placed on a flat surface and the molten salt poured into them. When the salt hardened, a flat surface was obtained which proved satisfactory for counting. It was found that better surfaces were obtained if the samples were poured on a hot (about 90°C) surface rather than one at room temperature. The hot samples also prevented the solidified salt from taking up water on the sample surface (this water made counting impossible to reproduce).

RESULTS

Rate of adsorption

The rate of adsorption data for calcium and strontium ions on alumina are plotted in Fig. 2 in terms of the fractional approach to equilibrium versus time. Since thallium was not adsorbed, it has not been plotted. The fractional approach to equilibrium is defined as $(C_i - C)/C_i - C_e)$, where C_i is the initial concentration on the cation, C is the concentration at any time, and C_e is the equilibrium concentration in the solution. All the solutions contained approximately 100 mg of cation per 100 g of solution together with 10 g of alumina. The runs were all made at 250 ± 5°C using the same stirring rate of about 200 rev/min in order to achieve the same hydrodynamic and mixing conditions in the 250 ml beaker.

Adsorption isotherms

The adsorption isotherms at 250°C are shown in Fig. 3, where the equilibrium adsorption of cation per gramme of adsorbent is plotted against the concentration of the cation in the solution. The data obtained for the calcium and thallium ions are correlated as a single, continuous line, while the data obtained for the strontium ion appear as a family of lines with the initial concentration of the solution as a parameter.

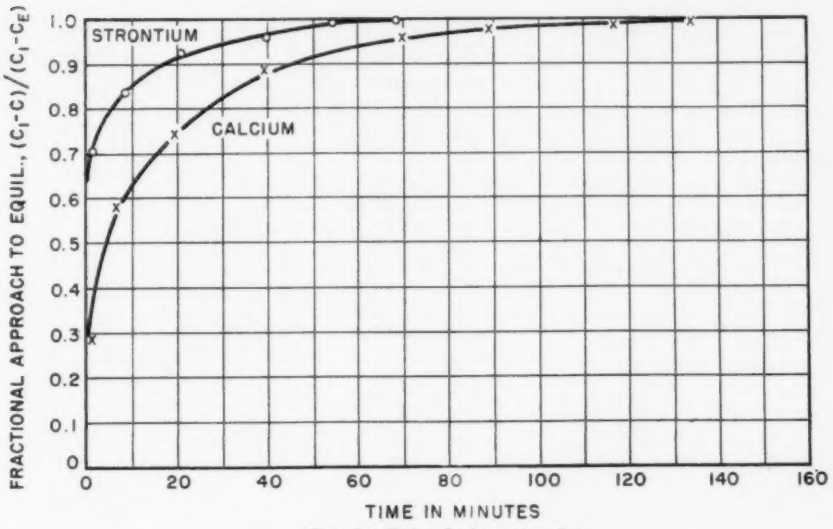

FIG. 2.—Rate of adsorption data.
Adsorbent alumina
Wt. alumina = 10 g
Temp. = 250°C
Stirring rate about 200 rev/min
Solution concentration

	Initial	Final
Calcium	100 mg/100 g	39·0 mg/100 g
Strontium	100 mg/100 g	83·2 mg/100 g

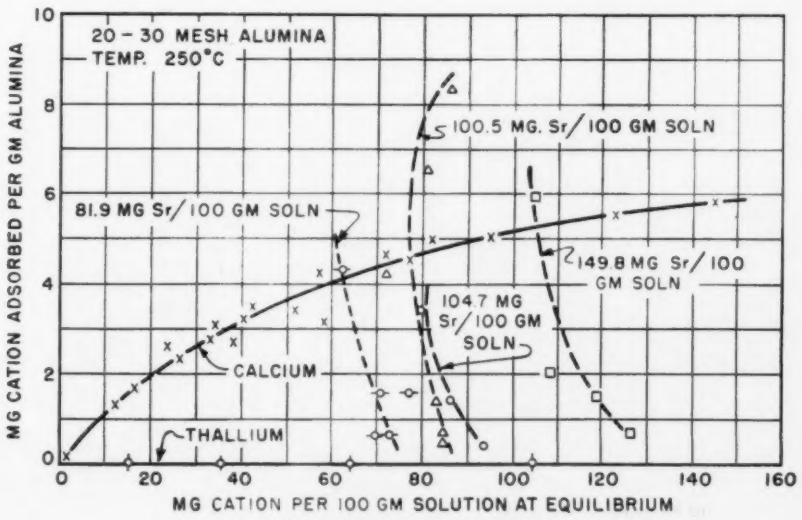
20 – 30 MESH ALUMINA
TEMP. 250°C
100.5 MG. Sr/100 GM SOLN
81.9 MG Sr/100 GM SOLN
149.8 MG Sr/100 GM SOLN
104.7 MG Sr/100 GM SOLN
CALCIUM
THALLIUM
MG CATION ADSORBED PER GM ALUMINA
MG CATION PER 100 GM SOLUTION AT EQUILIBRIUM

FIG. 3.—Adsorption isotherms.

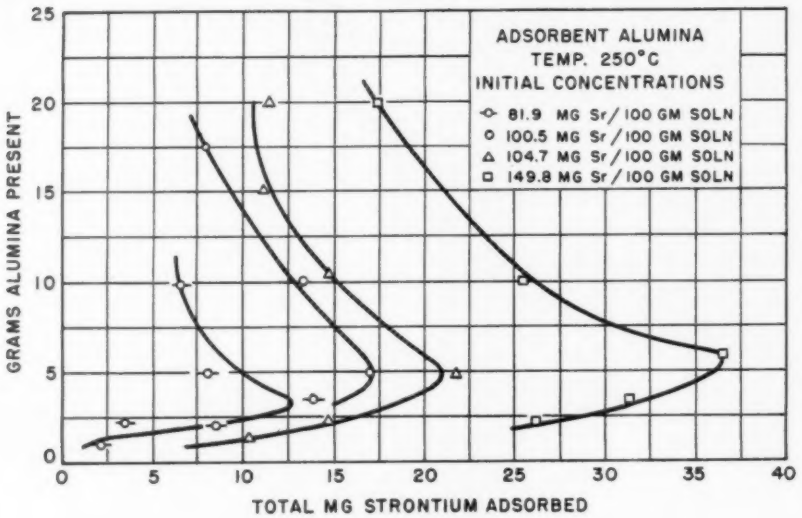

FIG. 4.—Strontium isotherm.

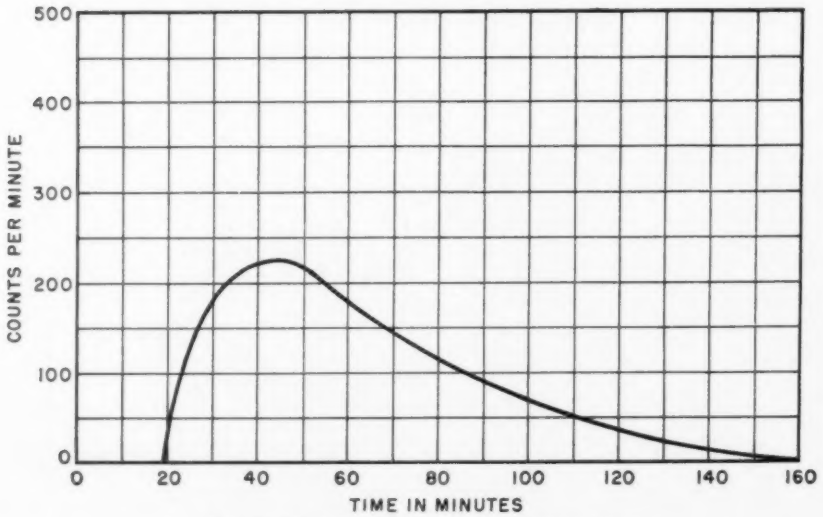

FIG. 5.—Elution curve of strontium through alumina.
Conc. of Soln. = 100 mg Sr/100 g Soln.
Volume of Sample = 35 ml
Initial counts per minute = 8000 (net)
Depth Bed = 39·7 cm
Temp. = 250°C
Vel. of Solvent = 14·3 mm/min.

It was necessary to plot the strontium results in this manner because obviously no single line was suitable. Due to the peculiar nature of the strontium data, an additional plot, Fig. 4, of total gramme of alumina present during adsorption versus total strontium ion adsorbed was made.

Adsorption in the packed bed

The original data for the adsorption column can be found in reference 10; an example of the curves obtained (smoothed values) is shown in Fig. 5. Elution analysis was used in practically all of this work. The counts/min are directly proportional to the concentration of the cations, and the appropriate information about the characteristics of the packed bed, the flow rates, and the solution concentration is given on the figure. The spread of the curve from an ideal front is due to both axial dispersion and the non-linear isotherms. Replacing the packing in the column seemed to have no effect on the results obtained.

Table 1 gives R values calculated by using various portions of the elution curve. R was defined as the velocity of the solute front through the packed bed divided by the

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TABLE 1.—SOLVENT VELOCITIES AND R VALUES

Run	Cation	Packing material	Solvent vel. mm/min	R Values		
				B.T.	½ Max	Peak
A	Ca	Silica	22·5	1·3	1·1	0·78
B	Tl	Silica	25·4	1·0	0·92	0·65
C	Ca	Alumina	20·6	1·1	—	—
D	Ca	Alumina	9·28	0·35	0·33	0·32
E	Sr	Alumina	14·2	1·5	1·1	0·67
F	Sr	Alumina	15·4	1·4	0·94	—
G	Tl	Alumina	15·5	1·6	1·2	0·97

TABLE 2.—CATION ELUTED FROM THE COLUMN

Run	Cation	Packing	mg Introduced	mg Eluted	Fraction eluted
A	Ca	Silica	12·0	11·3	0·94
B	Tl	Silica	35·4	31·0	0·88
D-1	Ca	Alumina	56·0	1·88	0·034
D-2	Ca	Alumina	1·02	0·0	0·0
D-3	Ca	Alumina	2·13	0·0	0·0
E	Sr	Alumina	107·0	16·6	0·155
G	Tl	Alumina	5·17	4·55	0·88

velocity of the pure solvent through the packed bed in consistent units. The R values are given for three portions of the elution curve: (1) when the first solute appeared in the eluate, or breakthrough (B.T.), (2) when the elution curve had reached one-half its maximum value, and (3) when the elution curve was at its maximum value or peak.

Table 2 gives the amount of cation introduced to the column for several runs, and

[10] T. L. ROACH. Thesis, The University of Texas (1960).

the amount of cation eluted from the column in each run. The weight of cation eluted was calculated from the elution curve by means of graphical integration.

DISCUSSION

The rate of adsorption plot, Fig. 2, indicates that under similar operating conditions the rate of adsorption of the strontium ion by alumina is considerably faster than that of the calcium ion. The rate of adsorption of the thallium is indeterminate since none was adsorbed, as shown in Fig. 3 by the straight line along the horizontal axis. The calcium isotherm seems to have the general form fitted by the Freundlich or Langmuir equation. The strontium data are most unusual in that they indicated more total strontium was adsorbed when less alumina was present. As can be seen from Fig. 4, the total amount of strontium adsorbed increased as the total gramme of alumina decreased until some "critical" weight of alumina was reached, at which point the adsorption curves turned back and approached zero adsorption for zero weight of alumina. This anomalous behaviour probably indicates that something else besides a pure surface phenomenon was taking place. One possible explanation is that some very minor impurity in the alumina formed a complex with the Sr^{2+} ion as the alumina quantity increased and prevented the Sr^{2+} ions from adsorbing on or reacting with the alumina.

It was found that great care had to be taken when collecting the strontium adsorption data. The foaming of the molten salt when it was stirred caused samples of solution to show a decreased count-rate. If a sample of solution with no adsorbent present was stirred rapidly for a while with the formation of a large amount of foam, a sample of solution containing no foam would show a considerably reduced count-rate. If the solution was then stirred slowly until all the bubbles had popped, the count-rate of the solution would return to its original value. This distribution phenomena has been observed in liquid foams, and perhaps offers the possibility of separating fission products by countercurrent "foaming" equipment.

In analysing the data obtained from the adsorption column, assuming that the value obtained for the void fraction of the bed was fairly accurate, it appeared that considerable longitudinal dispersion of the solute front took place in the packed bed. This in part caused the R values obtained to vary widely with material and velocity. VON ROSENBERG[11] has shown that when no adsorption takes place, the R value at one-half the maximum height of the elution curve should be unity. It can be seen from Table 1 that the R values at one-half the maximum for Runs A, B and G are approximately unity with a maximum deviation of 20 per cent.

R values present only one aspect of adsorption, namely a measure of "break through", and give no indication of total adsorption. Table 2 indicates the magniude of his effect. It was not possible to wash all the calcium and strontium ions from the alumina packing by passing pure eutectic through the bed even though it was possible to reduce the count rate of the eluate to background by washing (Fig. 5) and to reproduce data on the same packing. In the run presented in Fig. 5, 107 mg of strontium were introduced into the column while a graphical integration of the data revealed that only 16·6 mg were eluted. No effective way was found to elute the adsorbed strontium from the packed bed.

Calcium was the only cation that was actually completely held up in the adsorption

[11] D. U. VON ROSENBERG, *Amer. Inst. Chem. Engrs. J.* **2**, 55 (1956).

column for an extended time. When solutions containing 50 mg of calcium ion or less per 100 g of solution were run through the column with actual velocities through the bed of less than 10 mm/min, the calcium was held up on the column, giving an R of less than one. Also, a considerable amount of the calcium was held permanently on the alumina, and could not be eluted with pure eutectic. This seeming fixation of the Sr^{2+} and Ca^{2+} ions would indicate that some surface reactions as well as adsorption were taking place.

CONCLUSIONS

From the previous discussion the following conclusions can be drawn:

(1) Silica will not adsorb calcium, strontium or thallium ions from a zinc chloride–potassium chloride eutectic at 250°C.

(2) Thallium ions are not adsorbed by grade F-1, 20–30 mesh alumina under the conditions used in this investigation.

(3) Calcium and strontium ions are adsorbed to a considerable extent by grade F-1, 20–30 mesh alumina under the conditions used in this investigation.

(4) It appears that it might be possible to adsorb rather large amounts of calcium, strontium and chemically similar ions from molten salts in alumina packing.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 382 to 390. Pergamon Press Ltd. Printed in Northern Ireland

NOTES

Separation of carrier-free silver from rhodium metal foil*

(*Received* 13 *October* 1960)

THE only form of rhodium that will withstand the high temperatures generated by an internal cyclotron beam of ~16 MeV helium ions is the metal. Therefore it is necessary to start with rhodium foil in order to produce by an (α,n) reaction on ^{103}Rh enough ^{106}Ag for nuclear spectroscopy studies. The problem of dissolving the rhodium foil after a cyclotron bombardment is a difficult one; particularly when it is desired to separate carrier-free the silver produced.

The chemistry of rhodium has recently been reviewed by CHOPPIN.[1] An alkaline fusion can be used to convert the rhodium to water soluble $Rh_2(SO_4)_3$; or the metal can be heated in molten bismuth plus elemental carbon, the melt cooled and dissolved in HNO_3.[2] A large amount of unwanted chemicals is introduced into the target–product mixture by both these procedures.

The procedure that follows was developed to separate carrier-free ^{106}Ag for nuclear spectrographic studies. The large difference in the boiling points of rhodium and silver was taken advantage of to vacuum evaporate the ^{106}Ag from the molten rhodium target. An anion resin purification was also made; particularly to remove the ^{103}Pd produced by the $(d,2n)$ reaction on ^{103}Rh by the deuteron impurity in the helium ion cyclotron beam.

The relevant physical properties of rhodium, palladium, and silver are shown in Table 1.

TABLE 1.

Element	Melting Point	Boiling Point
Rhodium	1966°C	>2500°C
Palladium	1549	~2540
Silver	960	1950

Commercial rhodium foil, 0·003 in. thick, was used for the bombardments. Spectrographic analysis showed palladium and platinum impurities. A very thin, ≪0·001 in., layer of copper was electroplated on one side of the rhodium. The purpose of the copper was to provide a good base for soft-soldering the foil to the copper cyclotron probe; and it also made it easy to remove with acid the soft solder after the bombardment. This target arrangement would withstand an internal beam current of 16 MeV helium ions of at least ~100 μA for short periods, ~15 min; and it would withstand currents of ~80 μA for periods of days.

After bombardment the target foil was cleaned with acid and spot welded to a tantalum strip 1/4 in. wide and 0·015 in. thick. The target foil–tantalum strip was placed in a resistance heating assembly in a vacuum chamber, (see Fig. 1). A cylindrical quartz catcher was placed as shown around the resistance element. The rhodium was heated just to the melting point, or slightly below, and held there for a few seconds. Nearly 100 per cent of the activity was evaporated. In addition a very thin film, only slightly non-transparent, of rhodium was evaporated onto the inside of the catcher.

The activity and the metallic film were removed with a few drops of conc. HNO_3 plus one drop of conc. HF.[3] The metal was not appreciably dissolved, and it was discarded after centrifuging. The solution was evaporated to dryness and the activity taken up in 2 M HCl. Cl_2 gas was passed in to

* Work supported in part by the U.S. Atomic Energy Commission.

[1] G. R. CHOPPIN, National Academy of Sciences, National Research Council, Nuclear Science Series, NAS-NS 3008.

[2] Mrs. MAB I. TOCHER, Lawrence Radiation Laboratory, Private communication (1960).

[3] *Note*: Carrier-free silver has some tendency to stick to glass; therefore only plastic and quartz apparatus was used.

oxidize the impurities. It is important to oxidize the palladium to the (+4) state to increase its anion resin distribution coefficient.[4]

The 2 M HCl solution was passed through a Dowex-1 anion column, 3 mm × 2 cm, and the column was washed with several volumes of 2 M HCl. The silver was removed with 10 M HCl. The latter was diluted to 2 M in HCl and the anion column step repeated.

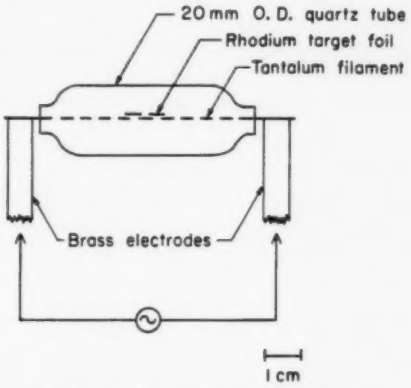

FIG. 1.—Resistance heated evaporation system.

The final HCl solution was evaporated to dryness. The activity was taken up in plating solution consisting of 2·5 ml conc. HNO_3, 2·5 ml conc. H_2SO_4, and 0·5 g of urea per 100 ml. The active silver was electroplated on a 0·010 in. platinum wire cathode. The plating was nearly 100 per cent complete after 1–2 hr with a current of 6 mA.

There was no discoloration or visible deposit on the wire after plating. The decay of one of the electroplated sources was followed with a Geiger–Müller counter for 8 half-lives. Only one component appeared; the half-life obtained by least-squares fitting was $8{\cdot}4_6 \pm 0{\cdot}1$ days. No conversion lines of the 40 keV transition in the decay of ^{103}Pd were observed on the spectrograph plates.

Quantitative tests were not made but the overall yield was ~50 per cent. The largest loss occurred in the up-take of the activity into the plating solution.

The author would like to thank Mr. J. B. MOORE for his assistance in the mechanical phases of this work.

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[4] U. L. SCHINDEWOLF, J. W. WINCHESTER and C. D. CORYELL, *Phys. Rev.* **105**, 1763 (1957).

Isotopic exchange of platinum between $[Pt(en)_2]^{++}$ and *trans*-$[Pt(en)_2Cl_2]^{++}$*

(*Received* 3 *November* 1960)

BASOLO *et al.*[1,2] reported that the isotopic exchange of chlorine between chloride ion and *trans*-$[Pt(en)_2Cl_2]^{++}$ (where "en" is ethylenediamine) was catalysed by the presence of $[Pt(en)_2]^{++}$ and that the rate was described by the expression

$$R = k[Pt(en)_2^{++}][Pt(en)_2Cl_2^{++}][Cl^-], \quad (1)$$

* Contribution No. 954. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

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[2] F. BASOLO, A. F. MESSING, P. H. WILKS, R. G. WILKINS and R. G. PEARSON, *J. Inorg. Nucl. Chem.* **8**, 203 (1958).

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where $k = 15\ M^{-2}\ sec^{-1}$. They proposed that the exchange occurs by a mechanism in which first the chloride ligand is added reversibly to an axial position of $[Pt(en)_2]^{++}$ to form $[Pt(en)_2Cl_2].^+$ The exchange is then effected by a transfer of a Cl^+ from $[Pt(en)_2Cl_2]^{++}$ to $[Pt(en)_2Cl].^+$ Simultaneously, the other chloride ligand from the $[Pt(en)_2Cl_2]^{++}$ is lost. They noted that this mechanism provides for the isotopic exchange of platinum and for the exchange of the ethylenediamine ligands between the two complexes, which will accordingly be chloride catalysed. They cited experiments in which *l*-propylenediamine (*l* − pn) was transferred from $[Pt(l - pn)_2]^{++}$ to $[Pt(en)_2Cl_2]^{++}$ at rates consistent with equation (1). Also, the rate for exchange of (en) between the two complexes, indicated by the use of ethylenediamine prepared from C^{14} tracer, has supported equation (1).[3]

The present work comprises the evaluation of exchange rates for Pt between the complex ions $[Pt(en)_2]^{++}$ and $[Pt(en)_2Cl_2],^{++}$ indicated with a ^{195}Pt tracer.

Experimental

The preparation and purification of the ^{195}Pt tracer have been described previously.[4] This reference describes equipment and technique for the measurement of the *K* X-ray intensity by a γ-ray scintillation spectrometer. The chlorides of the two cations were prepared by the method of Basolo *et al.*[5]

Table 1.—Data from exchange experiments

$[Pt(en)_2]^{++}$ M × 10^3	$[Pt(en)_2Cl_2]^{++}$ M × 10^3	Cl^- M × 10^3	$\tau_{1/2}$ min	k ($sec^{-1}\ M^{-2}$)
		For 25·0°C		
0·833	1·66	5·00	78	11·8
1·00	2·00	6·00	57	11·3
1·00	5·00	12·0	11	14·6
1·25	1·25	2·50	130	14·2
1·25	1·25	7·92	42	13·9
1·66	1·66	3·33	83	12·5
2·00	1·00	6·00	58	10·3
2·00	1·00	6·00	59	10·9
2·00	2·00	8·00	34	10·6
2·00	2·00	8·00	32	11·3
2·00	2·00	10·0	30	9·6
4·00	2·50	13·0	10·7	12·8
4·00	5·00	18·0	5·6	12·7
5·00	0·50	1·00	170	12·4
5·00	1·50	13·0	11·5	11·9
Ave. value				12·1 ± 1·4
		For 15°C		
2·50	2·50	10·0	36	6·4
2·50	1·25	7·5	63	6·5
1·00	2·00	10·7	56	6·4
Ave. value				6·4

A small quantity of the perchlorates was prepared for a few experiments with low chloride; however, considerable difficulty was experienced in obtaining pure perchlorates, and yields of pure materials were low.

For a separation of the two ions, the precipitation of $[Pt(en)_2]^{++}$ by the tetraphenylboron anion was used. Precipitates were washed with a solution of the $Na[B\phi_4]$ reagent. They were dissolved in acetone and reprecipitated by dilution with H_2O. Under a limited range of concentrations, the

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precipitate of the $[Pt(en)_3]^{++}$-salt formed rapidly and provided a clean separation. With an initial, careful purification of the two salts by fractional crystallization, any apparent initial or separation-induced exchange was less than 3–4 per cent. However, a slow precipitation of Pt^{IV} and the finite solubility of $[Pt(en)_3][B\phi_4]_2$ limited the concentration range which could be employed.

Exchange half-times were taken from the usual plots of $\log(1 - F)$ vs. t (where F is the fraction of exchange). In general, the plots were satisfactorily linear over a period that the exchange was followed, usually about two half-times. The experimental conditions and the results are presented in Table 1.

If the rate of the exchange is given by expression (1), the rate constant, k, is related to the half-time of an exchange experiment, $\tau_{1/2}$ by the expression

$$k = \ln 2/([Pt(en)_2^{++}] + [Pt(en)_2Cl_2^{++}])[Cl^-]\tau_{1/2}. \quad (2)$$

The indicated values of k are included in Table 1.

The results, which include a considerable range of concentration variables, confirm the form of rate expression predicted for the exchange by BASOLO *et al.*[1] The average value for k, 12·1 sec^{-1} M^{-2}, at 25° is 30 per cent lower than their value; however, with the statistics indicated in the table this difference may not be real. The limited number experiments at 15°C indicate values for the enthalpy and entropy of activation, $\Delta H^{\ddagger} = 10{\cdot}1$ kcal, and $\Delta S^{\pm} = -20$ e.u.

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Isotopic chlorine exchange between trimethylchlorosilane and hydrogen chloride

(*Received* 20 *October* 1960; *in revised form* 21 *November* 1960)

THE recently reported[1,2] study of the isotopic chlorine exchange between $SbCl_3$ and $(CH_3)_3SiCl$ prompts us to report some results on the isotopic chlorine exchange between gaseous HCl and liquid trimethylchlorosilane. The initial object of this work was an attempt to extend our earlier investigation[3] on the system $SiCl_4$–HCl to substituted silanes. As had been shown[4] by work with enriched $H^{35}Cl$, the halogen exchange with $SiCl_4$ is extremely slow at room temperature, but becomes readily measurable[3] in the neighbourhood of 90°C. In contrast, the halogen exchange between HCl and $(CH_3)_3SiCl$ in the gas phase at either 30° or 100°C is too slow to be conveniently measurable. A typical exchange run for $(CH_3)_3SiCl$ at $2{\cdot}48 \times 10^{-3}$ moles/l. and HCl at $4{\cdot}97 \times 10^{-3}$ moles/l. gave about 20 per cent exchange in 24 hr at 100°C.

These observations may be contrasted to the finding of BOGGS and BROCKWAY[5] who reported a decrease in the exchange rate between CH_3Cl and HCl when the hydrogens were successively replaced by more electronegative fluorine atoms.

Because the exchange studies on the gas phase system showed an appreciable (but irreproducible) "zero-time" exchange, it was decided to investigate the isotopic halogen exchange in the system HCl (gas)–$(CH_3)_3SiCl$ (liquid) since the separation method in the study of the gas phase system involved a transition through the inhomogeneous state.

Since the Henry's Law constant for HCl in $(CH_3)_3SiCl$ has not been measured, it is not possible to evaluate the kinetic parameters in terms of concentrations in the liquid phase. In order to establish the dependence of the exchange—which proved to be appreciably rapid, even at 0°C—on the hydrogen chloride concentration, the experiments were carried out in reaction vessels of constant volume (39·16 cm^3) and with a constant quantity of the liquid silane. Thus, assuming a linear relationship between the HCl concentration in the liquid phase and the total HCl pressure, the order of the reaction with respect to this component could be established.

[1] A. F. REID and R. MILLS, *J. Chem. Soc.* 703 (1960).
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A best fit plot of eight independent runs at a trimethylchlorosilane concentration of about 1·38 mmoles in the reaction vessel gives a first order (slope ~0·9) dependence on the HCl concentration. A typical set of data are summarized in Table 1. The root-mean-square deviation of the pseudo rate constant is ±18 per cent over a sixfold change in the HCl concentration. Assuming a first order dependence on the silane concentration as suggested by REID and MILLS,[2] the pseudo second-order specific rate constant is $4{\cdot}22 \times 10^{-3}$ mole^{-1} sec^{-1} at 0°C.

Despite considerable effort in reagent purification, rigorous exclusion of moisture and light, and use of an all-glass, stopcock grease-free system, the scatter of the data was rather severe. The reason

TABLE 1.—EXCHANGE DATA FOR THE SYSTEM $(CH_3)_3Si^{36}Cl + HCl$
Temperature: 0°C Volume: 0·03916 l.

Exp.	[HCl] (moles)	$[(CH_3)_3SiCl]$ (moles)	$t_{1/2}$ (min)	R (moles min^{-1})	$\frac{R}{k = [HCl]}$ (min^{-1})
44	$0{\cdot}697 \times 10^{-3}$	$1{\cdot}38 \times 10^{-3}$	$1{\cdot}07 \times 10^{2}$	$3{\cdot}00 \times 10^{-6}$	$4{\cdot}30 \times 10^{-3}$
48	0·717	1·37	1·73	1·89	2·63
49	0·454	1·36	2·12	1·11	2·45
50	2·00	1·39	0·79	7·20	3·60
51	1·94	1·39	0·73	7·70	3·97
52	2·73	1·39	0·59	10·8	3·96
				avg. $3{\cdot}49(\pm 0{\cdot}63) \times 10^{-3}$	

for this lack of replication may be that the reaction rate has a surface influenced component, as was found[5] true for the isotopic exchange reaction between CH_3Cl and HCl in which carefully outgassed (450°–500°C for 4 hr) reaction tubes resulted in very much slower exchange rates than were observed in untreated tubes. Because of this scatter it was not felt justified to pursue the present investigation in an attempt to establish more quantitative kinetic parameters. It is, however, interesting to note the qualitative implications of the observed exchange. From the results of ROCHOW *et al.*,[6] REID and WILKINS[7] and REID and MILLS,[2] it appears clear that ionic mechanisms based on the self-dissociation of trialkylchlorosilanes are probably not important in effecting the halogen exchange between $(CH_3)_3SiCl$ and $SbCl_3$, and it is probable that a similar situation obtains in the case of the silane as the primary solvent. A plausible exchange path thus presumably involves an activated complex in which the silicon atom exhibits a co-ordination number of five with a transition from sp^3 to sp^3d bonding. Such a transition state does not, of course, uniquely characterize the nature of the adduct, which presumably is undissociated hydrogen chloride with the hydrogen atom simultaneously bonded to the incoming and leaving chlorine atom. While the methylchlorosilane liquid phase has an appreciably polar nature, it should be noted that halogen exchange between the silane and HCl has also been observed in benzene solutions and thus the polar nature of the solvent can have, at best, only a small effect on the exchange rate.

The observation,[3,8] that no rapid isotopic halogen exchange between $SiCl_4$ and HCl or Cl_2 is noted under similar conditions must be taken as an indication of the greater ease of formation of the quinquevalent transition state for the trimethylchlorosilane, as compared to the tetrachloride. This view is consistent with the postulate[4] that at room temperature the very slow exchange between $SiCl_4$ and HCl proceeds through an $HSiCl_5$ intermediate, but at rates very much lower than those reported for the $(CH_3)_3SiCl$ system in the present work.

Experimental

Radiochlorine labelled $(CH_3)_3SiCl$ was prepared either by exchange with $H^{36}Cl$ or by exchange with $(CH_3)_4N^{36}Cl$ under anhydrous conditions as reported earlier.[9] All materials transfer was

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effected by the usual high vacuum techniques in thoroughly dried glass systems. The reaction vessel, which consisted of a 10 mm Pyrex glass ampoule provided with a filling arm (subsequently sealed off) and a break-off tip, was covered with opaque paint and a layer of aluminium foil to exclude light, and pre-treated with inactive chlorosilane (subsequently pumped off) to insure anhydrous conditions. The heterogeneous exchange runs at 0°C were carried out in an ice-water bath held in a large capacity Dewar flask. Complete liquefaction of the solid (liquid N_2 cooled) trimethylchlorosilane in 30 sec was noted in all runs. The reaction flask was shaken intermittently to insure mixing. At the end of the exchange run, the reactants were separated at −78°C and radioassayed, using the gas phase counting method described elsewhere.[10] Concentrations of the reactants were calculated on the basis of known gas dosage volumes, pressures and temperatures. No corrections for the solubility of HCl in liquid $(CH_3)_3SiCl$ were applied.

Part of this work was carried out at the University of Illinois. The support of the U.S. Atomic Energy Commission is gratefully acknowledged.

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Reaction of osmium tetroxide with iodide ions

(*Received* 26 *July* 1960; *in revised form* 14 *October* 1960)

THE reduction of osmium tetroxide by iodide ions in the presence of hydrochloric acid yields a variety of products. Earlier[1,2] it had been reported that four equivalents of iodine are produced, but the other reaction products were not identified; although one expects to obtain Os(IV) e.g. as $OsCl_6^{2-}$, the formation of improbable derivatives such as H_2OsI_4 had also been suggested.[3] After the removal of the iodine from the solution a dark green-blue solution containing the Os(IV) compounds remains. This investigation set out to identify the nature of these reduction products. The results are of interest because unusual mixed crystals with potassium hexachloro-osmate of a new chloro-iodo osmium IV complex are formed.

The reaction between osmium tetroxide and potassium iodide was carried out in hydrochloric acid solution to minimize hydrolysis and the iodine liberated was extracted with chloroform (see flow sheet). The yield of four iodine atoms per osmium tetroxide molecule was confirmed.[1,2] Extraction of the aqueous solution with ether removed a deep green ether-soluble compound but all attempts to isolate this as a solid material were unsuccessful. Decomposition occurred on evaporation under partial vacuum, even in the cold. Also, the green colour was destroyed when the ether solution was treated with drying agents; this ether solution contained osmium and iodine in the ratio 1:5, but no potassium. It was concluded that the green solute was probably $H[OsI_5.H_2O]$ or perhaps $H_2[OsI_5OH]$ but owing to its instability it was not further investigated.

By concentrating the aqueous solution until crystallization just began, two different crystalline substances were isolated, one soluble—subsequently shown to be potassium hexa-iodo-osmate (IV)—and the other insoluble in acetone. Small amounts of potassium chloride and iodide were removed by fractionation and the two substances then separated by treatment with acetone.

The acetone insoluble portion, analysed as $K_2OsCl_{5.75}I_{0.25}$ and at first a mixed crystal of K_2OsCl_6 and K_2OsI_6 was suspected. X-Ray powder photographs showed that the compound was cubic as for

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Flow Sheet

OsO_4 in 2·0 N HCl

Excess KI

Dark green solution

Extract with chloroform

$CHCl_3$ solution—Contains four equivalents iodine

Aqueous Residue

Extract with ether

Green ether extract: probably contains $H[OsI_5 \cdot H_2O]$

Aqueous residue: Concentrated

(*Acetone Insoluble*) Mixed Crystals of K_2OsCl_6 and $K_2OsCl_nI_{6-n}$

Acetone Soluble K_2OsI_6

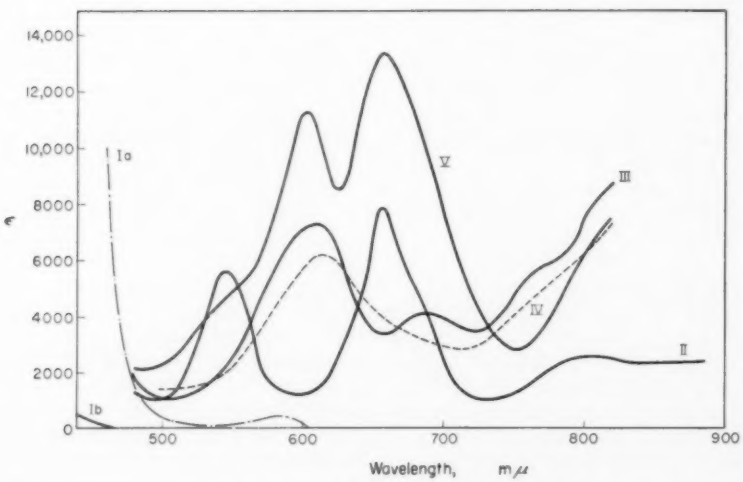

FIG. 1.—Visible spectra of: K_2OsCl_6 (Ia and Ib), K_2OsI_6 (II), K_2OsI_6 (0·044 g/l.) and K_2OsCl_6 (0·72 g/l.) (III), III one hour later (IV), $K_2OsCl_{5\cdot75}I_{0\cdot25}$ (0·72 g/l.) (V). The ε values for curve V were calculated assuming that all the iodine is present in the form of OsI_6^{--}. Spectra were taken within 20 min of the dissolution of the crystals and the solvent was 1·2 M $HClO_4$, except for II where a hydroiodic–perchloric solution was used. The values of ε for curve Ia must be divided by 100.

K_2OsCl_6 with $a = 9{\cdot}87 \pm 0{\cdot}02$ Å, the reported figure for K_2OsCl_6 being $9{\cdot}73 \pm 0{\cdot}02$ Å;[4] the increase in cell size was apparently due to the presence of larger iodide ions in place of chloride ions. The molecular weight calculated from these X-ray data and from the density is 511 ± 13. The average molecular weight for the formula $K_2OsCl_{5{\cdot}75}I_{0{\cdot}25}$ is 504.

Spectra have been found useful in establishing the nature of the mixed crystals. In Fig. 1 is shown the spectrum of K_2OsCl_6 (I) in 1·2 M perchloric acid; the absorption due to the $OsCl_6^{2-}$ ion above 500 mμ, the region where all other compounds absorb, is clearly negligible and hence can be ignored for our purposes. The spectrum of K_2OsI_6, however, depends critically on the time taken for measurement; a solution of K_2OsI_6($\sim 10^{-4}$ m) in 1·2 M perchloric acid is initially violet but decomposes in less than one minute to give a blue solution (III) which undergoes decomposition much more slowly. The spectrum of this solution after one hour is given in curve IV. The true spectrum of OsI_6^{2-} is given in curve II, excess iodide ions having been added; this violet solution is quite stable, the spectrum agreeing with that reported by JØRGENSEN[5]. Now the spectrum of $K_2OsCl_{5{\cdot}75}I_{0{\cdot}25}$ is given in curve V. This has been drawn by deliberately assuming (wrongly, of course) that all iodine is present as $[OsI_6]^{2-}$ ion, i.e. that the substance contains 4·5% K_2OsI_6. This assumption is clearly incorrect because curve V has a different shape from curve II and ε is too large, 13,400 as compared with 7800 for the true $[OsI_5]^{2-}$ ion. Furthermore, unlike the behaviour of $[OsI_6]^{2-}$ in solution the spectrum of the mixed compound $K_2OsCl_{5{\cdot}75}O_{6{\cdot}25}$ remained unchanged on standing in solution indefinitely; thus it is still blue-green after five days whereas a solution containing a mixture of K_2OsCl_6 and K_2OsI_6 changes rapidly in colour owing to aquation of the $[OsI_6]^{2-}$ ion as discussed above. Indeed it changes to a yellow colour after only 12 hr.

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Thus both the spectrum and the remarkable stability of $K_2OsCl_{5{\cdot}75}I_{0{\cdot}25}$ in aqueous solution rule out the existance of a discrete $[OsI_6]^{2-}$ group in the mixed crystal. We have come to the conclusion that the crystals contain a mixture of K_2OsCl_6 and a hitherto unknown iodo-chloro complex of the type $K_2OsCl_xI_{6-x}$. We believe that x is 3 or 4; this tentative suggestion is based upon the following argument. If we postulate that the band at 6·55 mμ has an ε value of about 7000–8000 as for OsI_6^{2-}, then one calculates $\varepsilon = 4500$ for $[OsCl_4I_2]^{2-}$ [i.e. (13400)/3], $\varepsilon = 6750$ for $[OsCl_3I_3]^{2-}$ and $\varepsilon = 9000$ for $[OsCl_2I_4]^{2-}$. The expected value of ε is thus intermediate between the values for $[OsCl_3I_3]^{2-}$ and $[OsCl_2I_4]^{2-}$. At best the above is a very empirical procedure.

The mixed crystal contains about 15% $[OsCl_4I_2]^{2-}$ if it is a di-iodo complex and about 9 per cent $[OsCl_3I_3]^{2-}$ if it is a tri-iodo derivative.

The compound is one of the few iodo-chlorides known and appears to be the first such compound of osmium, although several chloro-bromido mixed halides such as $OsCl_5Br^{2-}$ and $OsCl_3Br_3^{2-}$ have been reported among the platinum group metals.[6] All our attempts to prepare pure iodo-chlorides other than in these mixed crystals have been unsuccessful. Also, attempts to obtain a mixed chloro-iodide containing a different Cl:I ratio were unsuccessful. When the iodine concentration in the crystals is decreased the spectrum remains the same but the intensity is diminished indicating simply a smaller *yield* of the chloro-iodo compound. This strongly suggests that only one chloro-iodo complex ion is present in the crystals.

The value of the magnetic moment of the compound, determined at 20°C is 1·54 B.M. For comparison purposes we determined the magnetic moment of K_2OsCl_6 and the value observed (1·42 B.M.) agrees with previous work.[7]

Experimental

Iodide ion reduction

Osmium tetroxide, obtained by heating $K_2OsO_4.2H_2O$ (0·05 g) with 2 N sulphuric acid (20 ml) and sodium persulphate (0·5 g) was distilled into 4 N hydrochloric acid (60 ml) and treated with excess potassium iodide (1·0 g) in an inert (CO_2) atmosphere. The iodine was extracted with chloroform and titrated with thiosulphate. As the mean of several determinations $3{\cdot}97 \pm 0{\cdot}05$ equivalents of iodine were liberated.

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[7] D. P. MELLOR, *J. Proc. Roy. Soc., N.S.W.* **77**, 145 (1944).

Reduction products

Osmium tetroxide (2 g) in water (200 ml) was added to 4 N hydrochloric acid (200 ml) containing potassium iodide (20 g). The liberated iodine and the ether soluble compound were removed by ether extraction. The resulting turquoise blue aqueous solution was evaporated on the steam bath until crystallization began. On cooling the crystals (1·6 g) were filtered, washed with water to remove potassium chloride and iodide, then with 90% acetone and finally with pure acetone in which they are insoluble. (Found: K, 15·6; Os, 37·8; Cl, 39·7; I, 5·9%. $K_2OsCl_{5\cdot75}I_{0\cdot25}$ requires: K, 15·6; Os, 37·7; Cl, 40·4; I, 6·3. Further evaporation yielded more of this compound but eventually the acetone soluble K_2OsI_6 was obtained.

Analysis

Potassium was determined as potassium sulphate, and osmium by precipitating the element as the sulphide, then reducing this to the metal with hydrogen. Chlorine was determined gravimetrically, as silver chloride and iodine as palladous iodide, osmium having been previously removed by reduction to the metal with metallic zinc.

Iodine was determined as palladous iodine and chlorine obtained by weighing total halogen as (AgCl + AgI), the known iodine content being substracted.

Absorption spectra. These were determined with a Unicam SP 500 spectrophotometer, for the visible region. The solution required for the $OsI_6^=$ spectrum was prepared a few minutes before use by dissolution of potassium iodide (8 g) in 1·2 M perchloric acid (100 ml), potassium perchlorate being removed by centrifuging.

Infra-red spectra were measured in perfluorokerosene mulls, and were recorded on a Perkin Elmer 21 double beam spectrophotometer.

X-Ray results. X-ray powder photographs showed the unit cell to be cubic, $a = 9{\cdot}87 \pm 0{\cdot}02$ Å, the intensities of the lines being consistent with the fluorite-type structure. The density, measured by displacement of bromobenzene from a pycnometer, was $3{\cdot}53 \pm 0{\cdot}08$ g/cc. The molecular weight, assuming four molecules in the unit cell, is therefore 511 ± 13. Single crystals of the material were octahedral, and were not piezo-electric; X-ray rotation photographs showed only the spots characteristic of the fluorite structure (more strictly, in this case, the anti-fluorite structure), with no evidence of a lower symmetry. The X-ray evidence is thus consistent with a structure like that of K_2OsCl_6[4] with approximately 1 chlorine atom in 20 replaced by iodine, in a more or less random fashion, to give the effective formula $K_2OsCl_{5\cdot75}I_{0\cdot25}$.

Acknowledgements—A grant to one of us (A. T.) from the Italian National Research Council is gratefully acknowledged.

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J. Inorg. Nucl. Chem., 1961, Vol. 17, pp. 391 to 393. Pergamon Press Ltd. Printed in Northern Ireland

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Basic Chemistry in Nuclear Energy. Volume 28 of the Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. Geneva 1958. United Nations (1959) ix + 686 pp. $18,50,

THIS volume is a vivid reminder, if one were needed, of how great a part chemistry plays in the development of nuclear energy, from the isolation and purification of the starting materials without which the reactor will not work efficiently, to the processing, utilization and disposal of the products of fission. This book is composed of a collection of some 92 original papers dealing with a variety of chemical problems which are of interest and importance in the production of nuclear energy. There is however, in these papers, a great deal of valuable material which will be of interest also to inorganic chemists whose work lies in other fields.

The papers are divided into three groups. In the first part (28 papers) a variety of purely chemical topics are dealt with. Many of these are of wide interest. They include ten papers on various aspects of ion-exchange phenomena, on the chemistry or separation of ruthenium, technetium, rhodium, thorium, zirconium, niobium and polonium, and also contributions to the chemistry of fluorides and of fused salts in general.

The 22 papers which comprise Part II deal more particularly with the chemistry of the heavy metals and their compounds, especially those of interest to the production of nuclear energy, such as Thorium and Uranium. Ten papers deal with various aspects of the chemistry of the actinides. One realises, on reading these papers, that transmutation of elements has now become a factory process. In view of the opposition which has been expressed by some authors to the hypothesis of the existence of an actinide series, a critical review of the arguments concerning the position of these elements in the Periodic Table will of be general interest. Among the conclusions drawn by the author is that the lanthanide and actinide series are not part of Group IIIA but have their own individuality.

The 42 papers in Part III are concerned chiefly with matters of analysis, either of techniques associated with the analysis of materials involved in the production of nuclear energy or with the use of activation analysis for the determination of other elements.

F. FAIRBROTHER

The International Directory of Radioisotopes—I. Unprocessed and Processed Radioisotope Preparations and Special Radiation Sources. International Atomic Energy Agency, Vienna, 1959. iii + 264 pp.

IN this directory of radioisotopes the International Atomic Energy Agency has collected together all the information available to them about the world supply and distribution of radioisotopes. In undertaking a compilation of this kind the Agency must have been in the fortunate position where the suppliers were only too happy to furnish them with the information they required. A glance at the first nine pages of this volume, where over 45 suppliers are listed, confirms the international coverage claimed.

A brief list of definitions and explanations of terms used covers three pages and the remaining 264 pages are devoted to technical information on specific radioisotopes. For each isotope the available figures for half-life and energies of the radiations up to December 1958 are given, and in tabulated form the chemical form of the isotopes in question, the supplier, standard weight and the specific and total activity available.

The isotopes listed are arranged alphabetically rather than by atomic number as this has been found the most convenient method for quick consultation by isotope users in general. Volume I of this directory is a very useful source of reference on the supply of radioisotopes and together with Volume II, since published, which deals with labelled compounds containing carbon-14, hydrogen-3, iodine-131, phosphorus-32, and sulphur-35, deserves the attention of all users of radioisotopes.

R. J. MILLETT

Australian Atomic Energy Symposium, 1958. (Proceedings of a Symposium on the Peaceful Uses of Atomic Energy in Australia held in Sydney on 2–6 June, 1958). Melbourne University Press for the Australian Atomic Energy Commission, 1958. 788 pp., £5.10s..

Although this Conference was planned to take place only a few months before the Second Geneva Conference on Atomic Energy, it nevertheless attracted a large number of technical papers from all over the world. About half of them discuss Australian work and programmes, but the collected papers and the records of the discussions must be of interest to chemists, physicists, and metallurgists everywhere. It contains papers by authoritative authors on all aspects of a nuclear power programme from geology and mining, through extraction processes, metal production and alloy properties, ceramics, descriptions of many types of power reactors and experimental reactors, and on to chemical reprocessing and waste disposal. There are sections also on theoretical physics, radiation chemistry and nuclear chemistry, and the use of radioisotopes, and descriptive papers on radiation safety and techniques. The prospects for economic generation of nuclear power are discussed for United Kingdom, United States, Canadian and Australian conditions, though these discussions are not always incisive and are really only of value as background information for newcomers to the subject.

Many of the papers are surveys of relatively wide topics, but these are freely interspersed with papers of a detailed nature presenting new data for the first time. It is the presence of these papers that justifies the work of editing and publishing the Proceedings.

Of necessity such a book becomes dated, but it should be available as a reference work in all scientific laboratories which have any interest close to nuclear energy, for it gives within one volume a collection of quite recent information on all aspects of the nuclear energy industry.

K. D. B. JOHNSON

R. B. HESLOP and P. L. ROBINSON: **Inorganic Chemistry.** Elsevier, London, 1960. viii + 555 pp. 45s.

THIS book, as the authors state at the beginning of the preface, is addressed to students, and is intended to provide in a single volume an outline of current inorganic chemistry sufficient for basic reading up to honours degree standard. Ten chapters (200 pages) are devoted to surveys of general topics (the nucleus, radiochemistry, electronic structure of atoms, valency, stereochemistry, the solid state, chemical thermodynamics, chemical kinetics, and acids and bases); these are followed by twenty-seven chapters (300 pages) dealing with the chemistry of individual elements or groups of compounds (hydrides, oxides, halides, complexes and peroxy-compounds). A final short chapter, the position of which is perhaps of doubtful logical merit, gives brief accounts of ion exchange, partition chromatography, and solvent extraction.

The amount of information presented in readable form in this volume is astonishing, and the twenty-seven chapters on strictly inorganic chemistry constitute by far the best synopsis of that subject available at the present time. Frequent cross-references, tabular or schematic presentation of reactions and the liberal provision of very clear diagrams of structures help the student tremendously, and the inclusion of much very modern work (with indications of how recent it is) should do a great deal to stimulate interest in what undergraduates often fear will be a dull subject. A large number of references would be out of place in a book of this kind, and the authors have restricted citations (of which there are many) to authors' names and the years of publication; this is sometimes a pity, however, for it makes the location of several review articles which are suitable

at this level (and on which the authors have drawn freely) a matter of some labour, and the "suggestions for further reading" which are mentioned in the preface are too few in number to be useful.

There are, as is inevitable in the first edition of a work of this scope, a few errors. Redox electrodes are written in the American way (reduced form on the left) but given the European convention sign for the potential (e.g., Zn/Zn^{2+} $E^0 = -0{\cdot}76$ V), though the electrode reactions are written correctly (on the European convention) with the oxidized form on the left; it is therefore necessary to reverse the order of species for the electrode before the change from left to right has the correct sign for E^0 (and hence ΔG^0) for the electrode reaction. Iodates (p. 382) *do* contain IO_3^- ions: their deviation from the ideal perovskite structure has for some years been beyond doubt. Polynuclear carbonyls (p. 298) are generally believed to contain metal-metal bonds; dinitrogen pentoxide gives rise to two (not one) nitronium ions per molecule in sulphuric acid (p. 322); and the $TeCl_6^{2-}$ ion (p. 349) is *not* a distorted octahedron (a fact of great interest in valency theory).

These blemishes, however, detract only a little from the general quality of the book and, together with a number of printers' errors, will doubtless be corrected in a new edition. Production and binding are very good, and the price puts the volume within the reach of every student. The authors have made a major contribution to the teaching of inorganic chemistry, and the book is certain to remain a standard text for many years.

A. G. SHARPE

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A. A. SMALES and L. R. WAGER (Editors): **Methods in Geochemistry.** Interscience Publishers, New York, London, 1960. 464 pp., $13.50.

SEPARATED as they are by only a dozen miles of verdant landscape, the University at Oxford and the A.E.R.E. at Harwell have known each other for some time. We need not elaborate on the scientific resources available at these two institutions and so we should, perhaps, regard it as only natural that their symbiosis now produced a first-rate book on Geochemistry.

A valuable and important work, *Methods in Geochemistry* is the product of twelve authors: six from Oxford (BROWN, MAYNE, MOORBATH, TAYLOR, VINCENT and WAGER), five from Harwell (CORNISH, MAPPER, SHALGORSKY, SMALES and WEBSTER) and one (AHRENS) who is from Cape Town, but an Oxonian at heart. Together these writers have produced a thorough, concise, yet critical summary of the analytical procedures used in geochemistry today, with particular emphasis on the modern or "non-classic" aspects.

The first chapter, titled "Introduction", is actually a brief preface by the Editors, SMALES and WAGER. Chapter 2 deals with the handling and preparation of samples (including fluids) and the separation of their mineral constituents by physical and chemical means. The third chapter outlines the classic methods of major-constituent analysis and surveys flame photometry, colorimetry, turbidimetry and fluorimetry with a good evaluation of precision and accuracy. Spectrochemical analysis is treated in Chapter 4, briefly, clearly and carefully, and Chapter 5 explains the theory and growing applications of X-ray fluorescence. Chapter 6 is a brilliant summary of isotope geochemistry with a thorough technical discussion of the mass spectrometer. The detection of 10^{-43} g of uranium, reported on p. 194, is in itself a smashing accomplishment. Chapter 7 is an excellent review of isotope-dilution analysis, the related chemical procedures, possibilities and applications. In Chapter 8 Mr. MOORBATH harrows the well-tilled field of radioactivity, drawing on published material more than he should. If imitation is what the saying tells it is, then this reviewer should be most sincerely flattered. Chapter 9 gives a detailed review of neutron activation analysis and strives to demonstrate the broad applicability of this new technique and Chapter 10 is an abstract of the well-organized literature on Polarography. Chapter 11 discusses ion exchange, solvent extraction and chromatography, all of which have important applications in modern geochemistry.

The ten principal chapters have only 30–60 pages each, and some cover a lot of ground. Nevertheless, most of them penetrate well below the surface and thus allow the book to give a comprehensive view. We expect this book to find a broad audience and if we had to predict the area of its greatest influence we would mention graduate students and their teachers.

HENRY FAUL